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VOLUME 26 | SEPTEMBER 6, 1937 | NUMBER 18

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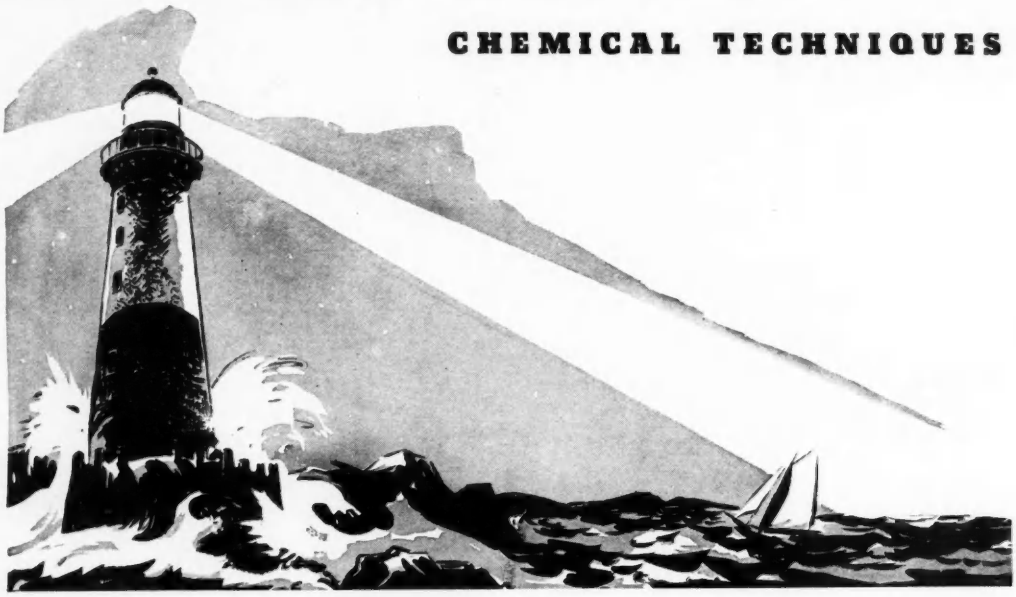

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VOLUME 26 | SEPTEMBER 6, 1937 | NUMBER 18

CONTENTS OF THIS ISSUE

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

General

Physical and Chemical Textile Testing—I 527
John H. Skinkle

Early Days and Early Ways of Dyeing 536
John Winters Fleming

Fractionation and Composition of Sulfonated Oils .. 549
Ralph Hart

Technical Notes from Foreign Sources 553

Meeting of American Chemical Society, Division of Cellulose Chemistry 554

Proceedings of
American Association of Textile Chemists and Colorists

Calendar of Coming Events P537

Photo, Annual Outing, Philadelphia Section P538

The Dyes of our Ancestors P539
Wm. H. Cady

Industrial Plant Design: Raw Stock Dyeing Machine. P543
A. L. Thomas

Control of Variables in Rawstock Dyeing P545
J. H. O'Neill

Outing, South Central Section P546

Unemployment Register P548

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AMERICAN
DYESTUFF REPORTER

VOLUME 26 SEPTEMBER 6, 1937 NUMBER 18

Physical and Chemical Textile Testing - I

JOHN H. SKINKLE*

INTRODUCTION

TEXTILE testing is carried out for one of several reasons and at several stages in the production of the goods. In general, we may say that testing is carried out in order to answer one or more questions:—Are the goods satisfactory? Are the goods better or poorer than another lot? What has been the effect of a certain process on the goods? If the goods are unsatisfactory or unusual, what is the cause of the abnormality? It will be seen that to answer all of these questions except the first involves a comparison of two samples, so that only to answer the first question are absolute standards and tolerances necessary. The answer to the first two questions is of interest primarily to the consumer; the answer to the last two questions is of interest to the manufacturer.

In this discussion of textile testing it is proposed to take up the test methods according to the following classification:

I. Physical Testing

- A. Statistical analysis
- B. Moisture determination
  1. Relative humidity—moisture in the air
  2. Regain—moisture in the textile material
- C. Fiber testing
  1. Staple—length of fiber
  2. Hair weight—thickness or bulk of fiber
  3. Resilience—springiness of fiber
- D. Yarn testing
  1. Counts—size of yarn
  2. Plies or filaments—number of strands in yarn.
  3. Twist—spirality of yarn
  4. Seriplane or regularity—evenness of yarn
- E. Fabric testing
  1. Yarn count—number of yarns per unit length or width
  2. Weight—weight of fabric per unit area
  3. Crimp—bending of yarns in the fabric.
  4. Thickness
  5. Porosity and waterproofing—penetrability of fabric to air and water
  6. Absorbability and wetting-out—ability to soak up liquids
  7. Heat insulation—ability to retain heat
  8. Abrasion test—wearing properties
  9. Stiffness and creasing — factors in draping qualities
- F. Strength and elongation testing of fibers, yarns, and fabrics

II. Chemical Testing

- A. Tests for content
  1. Ash and ash alkalinity—inorganic constituents
  2. Extraction analysis—oils, fats; waxes, soaps
  3. Sizing and weighting—stiffening and loading agents
  4. Union analysis—fibers present
  5. Acid or alkali content
- B. Tests for state or condition of textile material
  1. Cellulose fibers
     a. Baryta absorption—swelling
     b. Solubility in sodium hydroxide—damage
     c. Methylene Blue absorption—damage
     d. Copper number—damage
     e. Viscosity in cuprammonia—damage
  2. Animal fibers
     a. Nitrogen in wool and silk—damage
     b. Sulfur in wool—damage
     c. Ammonia nitrogen in wool—damage
     d. Solubility of wool in sodium hydroxide—damage
     e. "Soundness of wool"—damage
     f. Viscosity of silk—damage

III. Optical Testing

- A. Colorimeter
- B. Tintometer
- C. Colorimetric pH determination
- D. Refractive index
- E. Spectroscope and spectrophotometer
- F. Ultra-violet and infra red
- G. Microscopic tests

*Department of Chemistry, Lowell Textile Institute, Lowell, Massachusetts.

Where several methods are available the one considered best will be given in detail, and the other methods will be mentioned or considered in less detail. Very often approximate results may be obtained which are satisfactory for plant use or in a comparison and which require little or no special apparatus; these are especially valuable since many small plants cannot afford expensive apparatus, and even larger plants wish to make an occasional test of some sort, not usually performed because unnecessary, and which does not warrant the outlay of any great sum of money.

At the end of each test, a bibliography of references will be given where further information may be obtained.

PART I—PHYSICAL TESTING

CHAPTER 1—STATISTICAL ANALYSIS

In making physical tests on a textile sample, we are dealing with a very variable substance. If we make several determinations of strength, for example, on a piece of cloth we may find that no two tests give the same result. We may average the results, but how accurate is the average? Formulae have been developed based on the theories of probability which enable us to calculate not only the result desired but other very valuable information. The development of these formulae is too complex to follow but it is possible to use the formulae with comparatively little trouble. The following symbols will be used:

n=number of tests made
m=result of any one test
M=arithmetical mean of all the tests
d=deviation of any one test from the mean, regardless of whether it is plus or minus
sd=standard deviation of the tests from the mean
SE=standard error of the mean; the chances are 2 to 1 that the error involved in calling the mean the true value is less than this standard error

The formulae are as follows:

$$M = \frac{\Sigma m}{n}$$

$$d = M - m \text{ or } m - M$$

$$sd = \sqrt{\frac{\Sigma (d^2)}{n}} \text{ (square root of the mean square)}$$

$$SE = \frac{sd}{\sqrt{n-1}}$$

$$\text{True value} = M \pm SE$$

The standard error should never have more than two significant figures, and the mean should have as many decimal places as the standard error.

The use of the formulae can best be shown by a simple example. Let us suppose that we have made five strength tests on a piece of cloth and the results are:

$m_1 = 30.5$ lbs.
$m_2 = 31.2$ lbs.
$m_3 = 29.3$ lbs.
$m_4 = 30.8$ lbs.
$m_5 = 32.2$ lbs.

$\Sigma m = 154.0$ lbs.
$n = 5$ tests made

Then, $M = \frac{\Sigma m}{n} = \frac{154.0}{5} = 30.8$ lbs.

Calculating values of d and d^2

$d_1 = 30.8 - 30.5 = 0.3$ $d_1^2 = 0.09$
$d_2 = 31.2 - 30.8 = 0.4$ $d_2^2 = 0.16$
$d_3 = 30.8 - 29.3 = 1.5$ $d_3^2 = 2.25$
$d_4 = 30.8 - 30.8 = 0.0$ $d_4^2 = 0.00$
$d_5 = 32.2 - 30.8 = 1.4$ $d_5^2 = 1.96$

$\Sigma d^2 = 4.46$

Then, $sd = \sqrt{\frac{\Sigma d^2}{n}} = \sqrt{\frac{4.46}{5}} = \sqrt{0.892} = .946$

Then, $SE = \frac{sd}{\sqrt{n-1}} = \frac{.946}{\sqrt{5-1}} = .47$

The strength of the cloth then is 30.80 ± 0.47 or, in other words, the chances are very great that the true strength of the cloth is between 30.33 and 31.27.

The formulae may also be used to find out how many tests would be necessary to give a certain standard error.

The standard deviation expressed as percentage of the mean $\left(\frac{sd \times 100}{M}\right)$ is often used to express the variation of a piece of goods. In the example given the variation would be $\frac{.946 \times 100}{30.8} = 3.1$ per cent variation

Another use of standard error is to determine whether there is a real difference between two samples. The rule is: if the difference between two mean values is equal to, or greater than, twice the larger standard error, there is a real difference between the samples.

Suppose that a sample of the cloth already tested was boiled out in water and the strength determined as 29.90 ± 0.50

Then $30.80 - 29.90 = 0.90$

which is less than twice the larger standard error (0.50), therefore there is no difference in the strength and the treatment cannot be said to have injured the strength.

If on boiling with another liquid the strength had become 29.00 ± 0.40, then $30.80 - 29.00 = 1.80$ which is more than twice the larger standard error (0.47). In this case there is a real difference and the strength has been affected.

The following is a complete statistical analysis on an

experiment where a sample of cotton cloth was tested for strength before and after a certain treatment. It also illustrates the simplest form for calculating and tabulating results:

Before			*After*		
m	d	d^2	m	d	d^2
47.0	2.4	5.76	38.6	1.7	2.89
41.1	1.5	2.25	41.2	0.9	0.81
44.4	0.2	0.04	34.6	5.7	32.49
44.8	0.2	0.04	41.4	1.1	1.21
46.2	1.6	2.56	41.2	0.9	0.81
45.8	1.2	1.44	39.8	0.5	0.25
42.2	2.4	5.76	42.0	1.7	2.89
43.5	1.1	1.21	42.7	2.4	5.76
47.4	2.8	7.84	42.8	2.5	6.25
42.0	2.6	6.76	38.6	1.7	2.89
10|446.4		10|33.66	10|402.9		10|56.25
44.6		3.37	40.3		5.63

$sd = \sqrt{3.37} = 1.84$ $\quad SE = \frac{1.89}{\sqrt{9}} = 0.61$

Value $= 44.64 \pm 0.61$

Variation $= \frac{1.84 \times 100}{44.6} = 4.1\%$

$sd = \sqrt{5.63} = 2.38$ $\quad SE = \frac{2.38}{\sqrt{9}} = 0.79$

Value $= 40.29 \pm 0.79$

Variation $= \frac{2.38 \times 100}{40.3} = 5.9\%$

$44.64 - 40.29 = 4.35$

$\frac{4.35}{0.79} = 5.5$ therefore a real difference

CONCLUSION: There is a real difference between the strengths of the two samples. The variation in the sample after treatment is greater than before treatment. The treatment decreased the strength of the cloth and made it more uneven.

REFERENCES:

[1]Ezekial, M. Methods of Correlation Analysis. John Wiley & Sons, Inc., New York (1930).

CHAPTER 2—MOISTURE DETERMINATIONS

Relative Humidity

Perhaps the most important single factor in the physical testing of textiles is the amount of moisture in the air; affecting as it does the amount of moisture in the textile material, it thereby affects nearly every physical property of the goods.

The amount of moisture in the air may be expressed in one of three ways; (1) partial pressure, the actual pressure in inches of mercury due to the water vapor alone; (2) absolute humidity, the weight of the water vapor in a unit volume of air, usually in grains per cubic foot; (3) relative humidity, the percent saturation of the air, either one of the above compared to its maximum possible value at the temperature in question. It is with relative humidity that we are principally interested, since it seems to be relative humidity rather than actual moisture which affects the moisture in the textile sample.

Relative humidity may be defined by either of two equations:

$$RH = 100\ e/E$$

or $$RH = 100\ h/H$$

Where RH = relative humidity in %

e = actual vapor pressure in inches of mercury

E = maximum vapor pressure in inches of mercury

h = actual absolute humidity in grains per cubic foot

H = maximum absolute humidity in grains per cubic foot

The values of E and H may be obtained from Table I either directly or by interpolation, but the values of e or h must be determined experimentally.

TABLE I

Maximum Vapor Pressure and Absolute Humidities

Temperature ° F.	*Vapor pressure inches mercury*	*Absolute humidity grains per cubic foot*
32	0.18	2.12
35	0.20	2.38
40	0.25	2.86
45	0.30	3.44
50	0.36	4.11
55	0.44	4.89
60	0.52	5.80
65	0.62	6.85
70	0.74	8.07
75	0.88	9.46
80	1.03	11.06
85	1.22	12.88
90	1.42	14.95
95	1.66	17.30
100	1.94	19.97
105	2.25	22.97
110	2.60	26.34
120	3.45	34.37
130	4.53	44.36
140	5.89	56.69
150	7.58	71.74
160	9.66	89.99
170	12.21	111.9
180	15.30	138.0
190	19.02	169.0
200	23.47	205.3
210	28.75	247.8
212	29.92	257.1

The following methods may be used in determining relative humidity:

1. Chemical method
2. Dew point method
3. Hair hygrometer
4. Wet and dry bulb hygrometer
   a. Stationary type
   b. Sling psychrometer

The chemical method involves passing a measured volume of air through a drying agent such as phosphorus pentoxide or calcium chloride, the drying bulb being weighed before and after the experiment. The increase in

weight converted to grains and divided by the number of cubic feet of air passed through gives the actual absolute humidity (h), from which RH = 100 h/H, where H is determined from Table I. This method is the most accurate of any, more accurate than is necessary for textile purposes; it involves, however, the use of an analytical balance for weighing the moisture and an accurate meter for measuring the air, both of which are expensive and delicate, requiring a specially trained man to operate. Chemical methods, therefore, are seldom used in textile testing.

The dew point method is the next most accurate method. It consists in cooling a polished metal container of water down slowly until moisture just condenses upon its outer surface, this temperature being the dew point. The dew point is, then, the temperature at which the air would be saturated if cooled without loss of water vapor. An example will show best how relative humidity is calculated from dew points. Using Table I, assume that the temperature of the air in a room is 70° F. and its dew point, determined as above, is 50° F. The air would be saturated at 50° and would therefore have an absolute humidity of 4.11 grains per cubic foot (h); at 70°, the maximum possible absolute humidity is 8.07 grains per cubic foot (H).

Then RH = 100 h/H = 100 x 4.11/8.07 = 51%

As stated before, the dew point method is next in accuracy to the chemical method but since it requires considerable care to operate accurately and requires the use of a cooling medium, it is not very convenient for use in a plant.

The hair hygrometer is very frequently met with now, in the form of small table top or wall hygrometers; they operate by the change in length of a hair or band of hair acting through a link motion on a pointer. The stretch of a hair with change in relative humidity is approximately a straight line only over the middle portion of the scale, the response of the hair to changes in relative humidity is very slow, the link motion always has some play in it. For these reasons the hair hygrometer is the least accurate of the methods for determining relative humidity and requires frequent calibration if used at all. It is useful only for rough indications of rather large changes in relative humidity and should not be used for laboratory work.

The wet and dry bulb hygrometer operates on the principle that if we have a thermometer surrounded by a film of water and the air around it is not saturated, water will evaporate from the film at a rate proportional to the difference between saturation and the actual relative humidity. This evaporation requires heat which is taken from the bulb of the thermometer, so that the wet bulb thermometer will read less than the dry bulb thermometer by an amount inversely proportional to the relative humidity. It should be noted that the wet bulb reading is not the same as dew point.

The wet and dry bulb hygrometer is convenient and easy to manipulate, it is accurate to 1% relative humidity (fractions of a percent are not given), and so is much the most common type period of hygrometer used. There are two main types: the stationary and the sling psychrometer.

The stationary type has the thermometers fixed in position, the wet bulb moistened by a wick which dips into a container holding water, preferably distilled water. Since the air surrounding the wet bulb tends to be of higher relative humidity than the air of the rest of the room, it is desirable to fan hygrometers of this type before reading the thermometers. The Hygrodeik (Figure 1) is the most

Fig. 1—Hygrodeik Hygrometer

convenient instrument of this type, since a diagram and pointer for calculating the relative humidity is incorporated in the apparatus. Other forms of apparatus have a fan in the instrument for drawing air past the thermometers. These are desirable if so arranged that the heat of the motor does not affect the thermometers.

An instrument which is free of the stationary air film objection and yet uses the simple wet and dry bulb principle is the sling psychrometer (Figure 2). This instru-

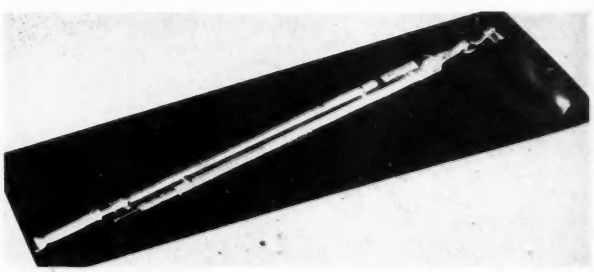

Fig. 2—Sling Psychrometer

ment consists of a pair of matched thermometers fastened to a rigid frame which can be whirled through the air. One of the thermometers is covered with a fine wick of silk, rayon, or mercerized cotton which is wet with distilled water before use. This instrument gives quick and accurate readings of the relative humidity but is not continuously recording. In wetting the wick, distilled water at a tem-

perature just above the wet bulb temperature (room temperature is satisfactory) should be used for reasons illustrated in Figure 3. If water colder than wet bulb is

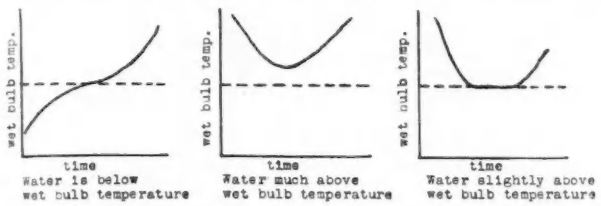

Fig. 3—Effect of Temperature of Water on Wet Bulb Reading

used, the temperature rises with only a point of inflexion at the wet bulb temperature; if too warm water is used, it is all evaporated and the temperature starts to rise again before wet bulb temperature is reached; if water only a few degrees warmer than wet bulb is used, however, the temperature drops rapidly to a long constant-reading minimum before rising again. The thermometers should be capable of being read to ¼° F. if the full accuracy of the instrument (the nearest 1% relative humidity) is to be realized; for plant use, however, thermometers accurate to ½° F. are satisfactory. The sling should be whirled at such a rate that the wet bulb has a linear velocity of 10-20 feet per second. After moistening the wet bulb with distilled water at room temperature, the instrument is whirled for 30 seconds and the thermometers read (wet bulb first, instrument held away from body); the instrument is then whirled for 20 seconds and read again; this is repeated until constant readings are obtained. The relative humidity may then be obtained roughly by Table II or more exactly by the data of Table I and the following formula:

$$e = e^1 - 0.000367\ P\ (t-t^1)\ (1 + \frac{t^1 - 32}{1571})$$

where, in addition to the symbols already used,

t = dry bulb temperature in 0° F.
t^1 = wet bulb temperature in ° F.
P = barometric pressure inches of mercury.
e^1 = maximum vapor pressure at t^1 (Table I)

As an example, suppose that the barometer is 30.0 inches of mercury, dry bulb temperature is 80° F. and wet bulb temperature is 70° F. Then

$$e = 0.74 - .000367 \times 30.0\ (80\text{-}70)\ (1 + \frac{70\text{-}32}{1571})$$
$$= 0.74 - .000367 \times 30.0 \times 10 \times 1.024$$
$$= 0.74 - .11 = 0.63$$
$$RH = 100\ e/E = 100 \times 0.63/1.03 = 61\%$$

From Table II, also, the value of the relative humidity is 61%.

Since temperature and relative humidity have such great effects on the physical properties of textiles, it is necessary that the conditions at which samples are tested be rigidly controlled. The effect of temperature is so small compared to the effect of relative humidity that it is usually neglected or, as will be seen later, compensated for by a small change in relative humidity. The usually accepted standard conditions are 70° F. and 65% relative humidity, the humidity being set at this comparatively high value because it is much easier to humidify air than to dehumidify it.

TABLE II
Relative Humidties by Sling Psychrometer

Wet bulb Depression	*Dry bulb temperatures—° F.*								
	60	65	70	75	80	85	90	95	100
2	89	90	90	91	91	92	92	93	94
4	78	80	81	82	83	84	85	85	86
6	68	70	72	74	75	77	78	79	80
8	58	61	64	66	68	69	71	72	73
10	48	52	55	58	61	63	65	66	67
12	39	44	48	51	54	57	58	60	62
14	30	35	40	44	47	50	52	54	56
16	21	27	33	37	41	44	47	49	51
18	13	20	25	30	35	38	41	43	46
20		12	19	24	29	33	36	38	41
22			12	18	23	27	31	34	37
24				12	18	22	26	29	32

The crudest way of obtaining a given humidity is to wet the floor and walls of a small room or set out open pans of water. This gives very little control and tests must be made very quickly while the air is at the desired humidity; since, as we shall see later, most textile material requires several hours to come to equilibrium with the atmosphere, this method is very unsatisfactory.

A method of obtaining constant relative humidity in a comparatively small space is to make use of the vapor pressure of various salts or saturated solutions of salts. More convenient still is the use of solutions of acids or salts which can be conveniently analyzed for composition, such as solutions of sulfuric acid, phosphoric acid, or calcium chloride. The writer has used solutions of sulfuric acid for this purpose, since the concentration of the acid can be easily determined by a simple titration. Table III gives the relative humidities corresponding to various concentrations of sulfuric acid.

TABLE III
Relative Humidities Above Sulfuric Acid Solutions

Relative Humidity %	*Concentration of Sulfuric Acid* % wt./vol.	*Relative Humidity* %	*Concentration of Sulfuric Acid* % wt./vol.
5	69.0	55	41.5
10	64.0	60	38.6
15	61.0	65	35.9
20	57.7	70	33.7
25	55.2	75	30.8
30	52.5	80	27.1
35	50.3	85	22.5
40	48.0	90	16.4
45	46.0	95	9.8
50	43.9	100	0.0

Best of all, if the amount of testing done warrants the expense is the use of hygrostats or psychrostats which control the wet and dry bulb temperatures automatically,

by adding moisture to the air in quantities just sufficient to keep the room at the desired humidity. The moisture is added to the air by means of sprays directly into the room (high up, at the ceiling) or by drawing air from the room through a compartment or cabinet where it is humidified by sprays and blown out into the room again; this last method is preferable because it gives a circulation of air which tends to eliminate dry or over-moist pockets.

The controlling element of the psychrostat or hygrostat may be one of two types. An older type which is still in use makes use of a filament of hair, viscose, or gut which lengthens with increasing humidity and so regulates a compressed air valve which in turn controls the sprays; this type of control is open to the same criticism as hair hygrometers, i.e., slow response to changes of humidity and frequent recalibration. A more recent type of control depends upon the use of two thermometer bellows, an atomizer spraying over one (wet bulb) draws air over the other (dry bulb); the dry bulb is connected by a link motion to the seat of a slide valve, and the wet bulb to the slide valve itself; the two act together to regulate the flow of compressed air which in turn operates the sprays of the humidifier.

The control of temperature is usually unnecessary although desirable if the volume of work done warrants it. Many types of thermostat are available and one should be selected which is applicable to the system of heating or cooling used. If the temperature does not vary more than 10° F., no regulation is necessary; if the variation is more than this, it may be compensated for by the following rules:

To maintain a constant amount of moisture in cotton goods increase the relative humidity 1% for every 10° F. above standard temperature.

To maintain a constant amount of moisture in woolen goods, increase the relative humidity 2% for every 10° F. above standard temperature.

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Regain

In expressing the amount of moisture present in a textile material, two methods of expression have been used: per cent moisture and per cent regain. Per cent moisture is used in the same way as any expression of percentage, that is, the weight of the component divided by the total weight of the sample and multiplied by 100. Per cent regain has been defined as the weight of moisture picked up (or regained) by 100 parts of dry material; this definition is misleading, however, in that this process is never carried out in the direction stated but always in the reverse direction. We shall define regain, therefore, as the weight of moisture in a sample divided by the dry weight of the sample and multiplied by 100. Per cent moisture is used mostly by chemists, per cent regain is used mostly by textile technicians. To express the results in formula form:

Let a = weight of sample with moisture
b = weigh of sample after drying
M = % moisture
R = % regain
Then

$$M = \frac{100\ (a-b)}{a} \qquad R = \frac{100\ (a-b)}{b}$$

The interrelationships of M and R are shown by the following:

$$R = \frac{100M}{100-M} \qquad M = \frac{100R}{100+R}$$

Obviously, then, if we know either M or R, we may find the other. Also, of three quantities a, b, and R; if we know any two we may find the third:

$$a = b\ (1 + R/100) = b\ \left(\frac{100+R}{100}\right)$$

$$b = \frac{a}{1+R/100} = a\ \left(\frac{100}{100+R}\right)$$

There are four principal methods which have been used for the determination of regain:

1. Xylol method
2. Relative humidity in equilibrium with sample
3. Vacuum dessicator with drying agent
4. Drying ovens
   a. Low temperature, using dry air
   b. High temperature, using air from room

The first three of these methods are comparatively unimportant. The xylol method depends upon distilling from a flask containing the sample and a large volume of xylol; the moisture distills over with the xylol and may be collected in a measuring tube or graduate; this method requires a large sample, bulky apparatus, and recovery of the xylol used. The determination of relative humidity in equilibrium with a sample as a measure of the regain of the sample has been used for quick but rather inaccurate determinations. One method is to place the sample in a sealed vessel with a hygrometer attached. Another method is to place the sample in a closed circuit through which air is circulated, a hygrometer reading the relative humidity. The third method was used by Urquhart in making the most accurate regain determinations yet made; a dessicator containing phosphorus pentoxide held the sample and the whole was then evacuated; at the end of a week the moisture had been completely removed from the sample. This is the most accurate method but the time required makes its use impractical for industrial purposes.

The oven method is the best method to use, considering both factors of accuracy and speed of determination. Using the oven method at temperatures of 220-230° F. (105-

110° C.) air from the room may be used to dry the samples. This is preferable in most cases to the low temperature method of using dried air at 140° F. (60° C.) because it avoids the use of air drying apparatus which must be constantly renewed, it is quicker, and it is as accurate as the low temperature method when only the textile material is present with or without the usual additional substances. In a few cases, where certain substances are present on the material, such as certain more volatile oils or substances which might react with the fiber at high temperatures, the low temperature method is desirable; on the whole however, the high temperature oven may be considered as the standard method of obtaining regain.

Using the high temperature oven, the time required to reach dryness varies with the type of fiber and weight of fabric. All fabrics have a drying curve similar in shape to Figure 4, which shows that most of the moisture is lost

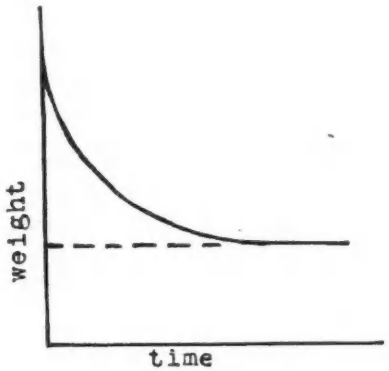

Fig. 4—Drying Curve

very rapidly but that the last portions are held rather tenaciously by the fiber. In all ordinary cases, drying is complete in one hour, but 1½ hours should be allowed for safety; better still, fabrics should be dried to constant weight, that is, until two weighings 10-15 minutes apart show no further loss in weight, in the case of some heavy fabrics or felts, this may be a very long time. If we compare regains obtained in this way with regains obtained by the more accurate but very slow vacuum dessicator method we find that, in the oven, wool does not lose quite all of its moisture whereas cotton loses a little more weight than there is moisture present; this excess loss is not due to decomposition of the cotton however but is due to volatilization of some of the impurities present— in cotton which has been boiled out or bleached thoroughly this loss of weight is insignificant. In view of the fact that exactly the true regains are not given by the oven method (although the error is very small), there is a growing tendency to refer to samples dried in the oven as "oven-dry" rather than the old term "bone-dry."

There are two general procedures used in determining the dry weight of a sample:—

1. Dry in the oven, transfer to weighing bottle, weigh on balance outside oven.
2. Dry in oven and weigh while still in oven.

The method to be used will depend upon what apparatus is available. The ordinary chemical drying oven (Figure 5) is to be found in nearly all chemical laboratories and is

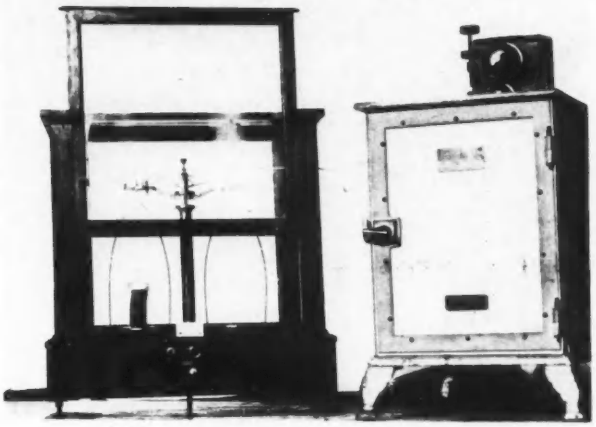

Fig. 5—Separate Oven and Balance

very cheap and easy to use; the analytical balance is also to be found in any well equipped chemical laboratory. The weighing bottle (a glass capsule with a ground glass stopper) is dried, cooled in a dessicator, and weighed; this weight is a constant and may be recorded in the laboratory log-book opposite the number of the weighing bottle. The sample is placed in the weighing bottle, and the whole placed in the oven with the cover of the weighing bottle off (usually tipped over at right angles); after drying the required length of time, the cover of the weighing bottle is placed in position, the weighing bottle and contents are cooled in a dessicator and then weighed on a balance. On subtracting the weight of the bottle, the dry weight of the sample is obtained. This method does not readily lend itself to progressive weighings to determine when constant weight is reached and also there is a possibility of picking up moisture during the weighting, but it has the advantage of using apparatus which is ordinarily present in a laboratory.

A better procedure when the apparatus is available is to weigh the samples while still in the oven. The apparatus ordinarily sold and used for this purpose is a combination oven and balance accurate to one centigram or to one-eighth of a grain (Figure 6); but where chemical testing is also to be done, or where it will be necessary to work with small weights of sample, or where small differences in weight will be measured, it is much better to have a combination oven and analytical balance (Figure 7). In this type of apparatus, the balance is mounted on top of the oven, a rod attached to the left hand pan of the balance passes down through an opening in the top of the oven and ends in a hook on which may be hung one of a number of baskets of the same weight. A counterpoise equal in weight to the rod and basket is placed on the right hand pan of the balance. The sample is placed in a basket, dried in the oven, and weighed by the balance at the end of an hour,

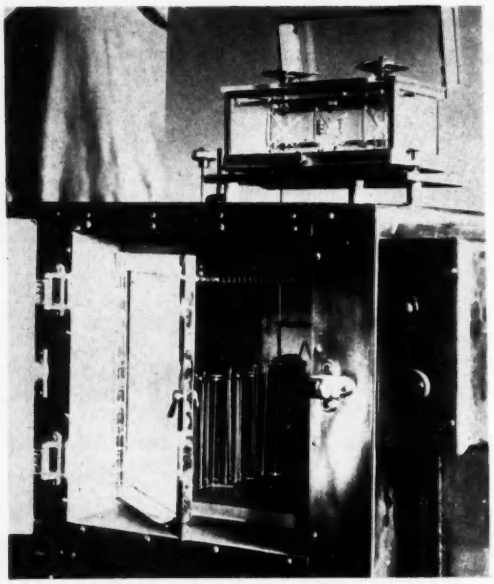

Fig. 6—Oven and Balanced Combined

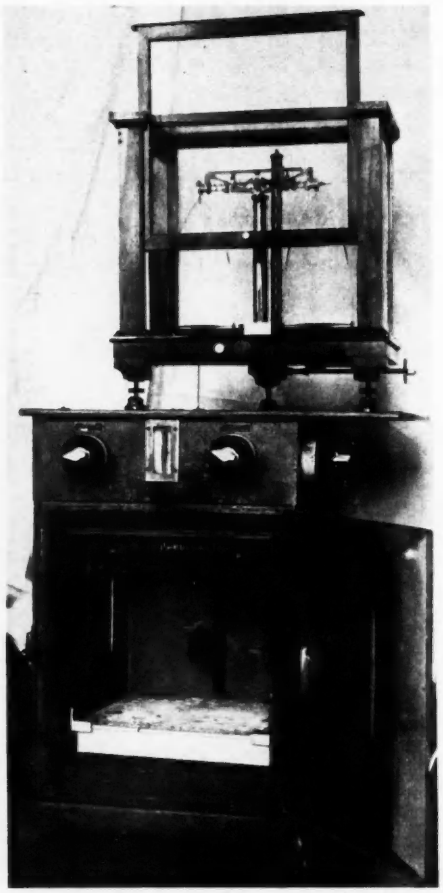

Fig. 7—Oven and Analytical Balance

the weighing is then repeated at 10 or 15 minutes intervals until constant weight is reached—this is the oven dry weight. If an analytical balance is used, one of the chainomatic type is very desirable for quicker weighing and the absence of small weights.

The effect of relative humidity upon regain may be best shown by a graph (Figure 8). This shows for any one

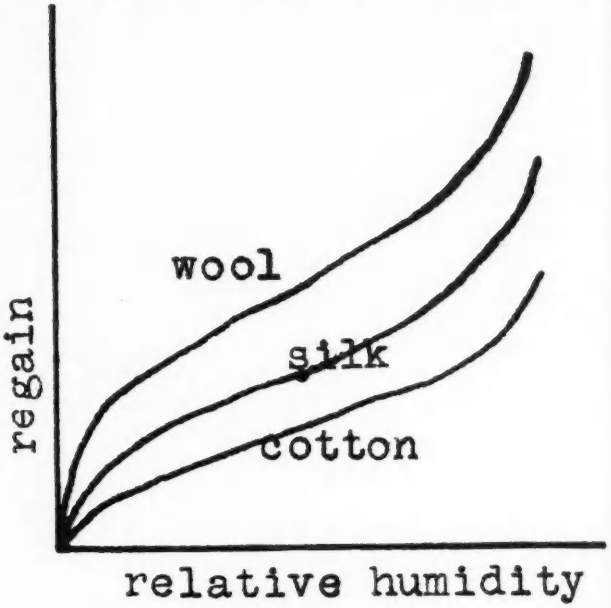

Fig. 8—Effect of Relative Humidity on Regain

material, starting with dry air, the addition of only a small amount of moisture to the air results in considerable increase in regain; then follows a period, which is almost a straight line, in which the regain is proportional to the relative humidity; finally, when the air is nearly saturated, further additions of moisture to the air results in large increases in regain. A colloid chemist would immediately recognize the shape of this curve as typical of the process of adsorption of a vapor by a rigid porous gel such as silica gel, stannic oxide gel, or charcoal. Since the moisture is being adsorbed from a mixture of air and water vapor, a colloid chemist would also expect the phenomenon of hysteresis, and accurate determinations have shown that hysteresis occurs (Figure 9). Hysteresis is a general term

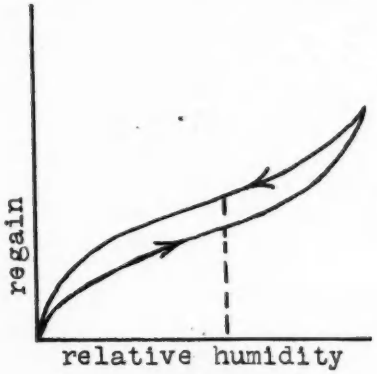

Fig. 9—Hysteresis Effect

applying to many branches of science and refers to the phenomenon of obtaining different results in a process according to the direction from which we approach equilibrium. In this particular case hysteresis manifests itself as two different values of regain for a material in contact with air of a certain relative humidity depending whether we start with the fabric drier or moister than equilibrium. If we are testing a sample of wool at standard conditions (70° F, 65% RH) and start with dry wool, we will find that the wool will not pick up more than 14.5% regain. The same sample of wool, if moistened and allowed to come to equilibrium will not have less than 16.5% regain. This difference in regain would cause considerable difference in the physical properties, so that it is not enough to say what standard conditions are—we must also say how we reach standard condition. The generally accepted method is the one specified by the A.S.T.M.—"moisture equilibrium shall be approached from the dry side."

As shown in Figure 10, the effect of temperature on

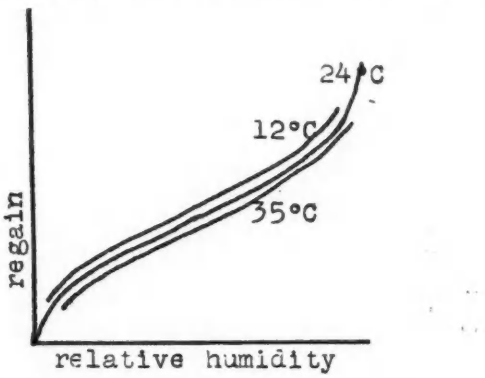

Fig. 10—Effect of Temperature on Regain

regain is comparatively small when the temperature is around room condition. As indicated in the discussion of relative humidity, temperature changes of 10° F. or more are generally compensated for by a small change in relative humidity; temperature changes of less than 10° F. are negligible.

Textile materials exposed to standard conditions of temperature and relative humidity will require varying periods of time to come to equlibrium. If the material is loose fiber, loosely twisted yarn, or a light porous fabric two hours is sufficient; heavy duck may require up to six hours; samples of hard felt have taken weeks and even months. In order to be certain that equlibrium is reached, it is wise to weigh a small piece of material at intervals until no further increase in weight occurs, after which the material is in equilibrium.

The previous treatment of the sample and its mechanical form also affect the regain. Cotton taken from the interior of a bale, or wool from the interior of a hard felt, have considerably less moisture than samples not under pressure. Cleansing treatments also alter the regain; for example, at 60% relative humidity and 25° C. raw wool had a regain of 10.9%, the same wool after washing had a regain of 13.7%, after combing of 13.0%; a raw silk had a regain of 7.7%, after degumming the same silk was 10.5%; a sample of cotton had a regain of 7.3%, after bleaching it had 6.3% regain. Conversely, oiling wool which is to be combed decreases the amount of moisture which the wool can hold at any given set of humidity conditions. Whether the material is in the form of loose fiber, yarn, or cloth also affects the regain; for example, at standard conditions loose cotton will hold 8.5% regain, cotton yarn 7.0 to 7.5%, and cotton cloth about 6.5% regain.

TABLE IV

Standard Regains of Textile Materials

Cotton fiber	8.5%
Cotton yarn	7.0
Cotton cloth	6.5
Mercerized cotton yarn	8.5
Acetate rayon	6.5
Viscose, cupra, nitro rayons	11.0
Silk	11.0
Mohair	10.0
Camel hair	13.0
Wool fiber, scoured	13.6
Woolen yarn	13.0
Worsted, oil spun (Bradford)	13.0
Worsted, dry spun (French)	15.0

Table IV gives the standard regains for various fibers in various mechanical forms. These standard regains are approximately the regains of the fibers at standard conditions of 70° F. and 65% relative humidity. The values are those which have been officially adopted where this is possible, in a few cases the values which are generally accepted but which are not official are given.

Since the regain is affected by so many variables, it is obvious that its effect must be eliminated in some way during the testing. This has been done in the following manners:

1. Testing "bone dry."
2. Testing wet.
3. Testing at standard conditions (or standard regain).
4. Testing at room conditions, measuring the regain, and correcting to standard regain or to a bone dry condition.

Testing "bone-dry" is impracticable for such determinations as strength or twist because of the instant rapid adsorption of moisture that occurs as soon as a sample is exposed to the air. Weighings, however, are most accurate when made "bone dry"; all chemical tests are based on oven-dry weighings and such determinations as counts of yarn or weight per unit area of cloth are most accurately made if the weighings are made when the sample is oven-dry.

Testing in the wet condition, especially strength and stretch testing, was very common in the early days of textile testing when the effect of relative humidity was known but nothing had been done to allow for it. The

results obtained, however, were not always comparable with the results obtained under normal conditions, so that the practice is obsolete now except for the case of rayons which are tested for strength both wet and at standard conditions.

Testing at standard conditions or at standard regain is by all means the most accurate and convenient except for weighings, which are better done in the oven dry condition. Expensive apparatus for the control of humidity is necessary, however, and small plants or laboratories where textile testing is not done in large amounts may get along very well by testing at whatever conditions prevail and correcting to standard conditions. In many chemical processes, especially, the effect of a certain treatment is shown by testing a sample before and after the process; since a comparison is all that is necessary, standard conditions are not necessary. Testing can also be carried out at conditions other than standard by testing a standard sample at the same time and referring all other tests to this sample. In chemical testing, very often two samples are weighed out at once; on one sample the test is carried out, on the other sample a moisture determination is made; the test sample is then corrected for the regain found in the second sample. This is done, for example, in the case of copper number determinations because heating a sample to get the dry weight might cause more oxy cellulose or hydrocellulose formation than is really present at room conditions.

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(To be continued)

Early Days and Early Ways of Dyeing

Miniature Models Portray Ancient Dye-House in Operation in Unique Museum Exhibit.

John Winters Fleming

EXTRACTION of dyestuffs and the art, science and business of dyeing are represented as one of man's earliest industries in a new, permanent and unique exhibition, titled Early Industry, in the Knox Hall of Civilization at the Buffalo Museum of Science, Buffalo, New York.

Miniature cast wax models of ancient man and his primitive implements and raw materials portray an early dye-house in operation with lilliputian figures shown breaking shells, extracting dye veins, boiling the dyes in water and applying them to mats and yarns. The models, exactly and exquisitely molded in perfect proportions and relationships, were made by museum preparators in the museum's division of preparation under the direction of Dr. Carlos E. Cummings, museum director. Early days and early ways in twenty-two different industries are depicted in the exhibition.

Several centuries before the Christian Era dyeing reached a state of perfection. So much so, it is said, that the most modern scientific processes have failed to improve upon the famous purple dye processed in the ancient, Biblical City of Tyre in 1000 B.C. Tributes to this dye still live in our speech in such expressions as "born to the purple" and "the royal purple." The ancient peoples used equipment, materials and processes similar to those in use today. Their equipment was simple, comprising vats, kettles, and cisterns of wood, iron and stone.

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

SEPTEMBER 6, 1937

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Calendar of Coming Events

Fall Meeting, Piedmont Section, Carolina Hotel, Pinehurst, N. C. November 6, 1937.

Annual Meeting and Convention, December 3 and 4, 1937, Bellevue-Stratford Hotel, Philadelphia, Pa.

Dinner at Annual Outing, Philadelphia Section, Whitemarsh Valley Country Club, Whitemarsh, Pa., May 14, 1937.

The Dyes of Our Ancestors*

WM. H. CADY

IN these strenuous modern days when textile chemists and colorists in addition to their usual burdens in connection with the production of more or less permanent colors are loaded up with a lot of specialties such as waterproofness, mildewproofness, crease resistance, fire resistance, Trubenizing, Sanforizing, lustering and delustering, to mention only a few, it is pleasant to relax at the end of a busy week and turn time backward a few centuries to the period when happily not any of these newfangled notions had even been suggested, and if they had been, there were no textile chemists to work on them, and as for the dyers, they were too much occupied with trying to keep out of jail to have any time left for such abstractions as "consumer appeal" or such slogans as "permanent while the fiber lasts." On the contrary, if the product of their tinctorial efforts bore any label at all, it probably read "Without Guarantee."

In this brief sketch we will make no attempt to cover the entire subject; it would be as difficult to condense a history of dyeing into a half hour's talk as it would be to crowd a hoop-skirt into a suit-case. Instead, we will merely hit a few of the high spots, and try to show you some of the difficulties besetting the old-time dyer, working with only a handful of colors, in the crudest of apparatus, and frequently hampered by laws which absolutely forbade the use of his favorite dyes. Perhaps after hearing this brief story some of you who are dissatisfied with modern conditions may find that there is something to be thankful for after all.

So I propose that we forget tonight the dyes to which we are accustomed, and which are so simple in their application that most anybody can be a dyer if he possesses an eye for color and a can-opener, and that we think of a past and almost forgotten era when dye powders in tin cans were as unknown as the radio and the automobile, and when dyeing formulas were family secrets, transmitted from father to son as a valuable inheritance, and not obtainable by the public at large at any price.

Let us get back to the beginning of dyeing, or as near the beginning as the records will carry us.

If I should want a text for this discourse, I should find it in the book of Genesis, chapter 37, verse 3: "Now Israel loved Joseph more than all his children, because he was the son of his old age; and he made him a coat of many colors." The average person probably imagines that this garment, the most famous bit of men's wear in all history, was constructed along the lines of the old-fashioned crazy-quilts such as our grandmothers used to make, containing all the spectral colors and others besides. Unfortunately this is quite improbable, because there seem to have been only about three dyes known to the Hebrews in Jacob's time (around 1700 B.C.), namely blue, purple and scarlet. It should be explained that at this particular time (1700 B.C.) the art of dyeing had already made considerably more progress in some other parts of the world, and particularly in Egypt, but as the Hebrews were not on speaking terms with the Egyptians, naturally they knew nothing of all this; though when they were carried into captivity by the Egyptians a few years later, they doubtless learned plenty.

But to get back to those three colors on Joseph's coat. This color scheme, blue, purple and scarlet, a sort of composite of Yale, Holy Cross and Harvard, is mentioned frequently in the Old Testament, particularly in Exodus in connection with the specifications for the Tabernacle. Elsewhere we read of "a cloth wholly of blue," "a cloth of scarlet," "a garment of divers colors . . . for with such robes were the King's daughters that were virgins appareled," and so on. Now to take up these "divers colors" one at a time; there is reason to believe that the blue was the same as our present-day Indigo, or as we would say, a medium shade of navy; the scarlet came from an insect called "Kermes," belonging to the Cochineal family, and probably was a rather dull red in reality; and the purple was without much doubt the celebrated but overrated Tyrian Purple, which may have been anything from a reddish blue to a lavender.

Purple has always been the symbol of authority. Homer tells us that it was worn only by princes, and we read in the Bible of the purple raiment of the kings of Midian and the purple garments of the high priests. The Babylonians and other nations arrayed their gods in robes of the same color.

Tyrian Purple, as you might infer from its name, was discovered in the ancient city of Tyre. According to a Greek legend, the discovery came about in this fashion. Hercules was walking along the seashore, accompanied by his dog. The animal came upon a shell-fish, and having the usual canine appetite, started to devour it. Instantly, according to the fable, "an indelible purple stained its muzzle," which color was afterwards applied to the dyeing of wool with great success.

*Presented at a meeting of the R. I. Section, A.A.T.C.C. Feb. 26, 1937, and at a meeting of the Northern New England Section, A.A.T.C.C., March 5, 1937.

According to Pliny, to whom we are indebted for most of the scanty information we have regarding ancient dyes, there were several kinds of Purple, one "faint, approaching to a scarlet," another a very dull red "approaching to a violet" and a third resembling coagulated bullock's blood; all obtained from different varieties of shell-fish. Some were found on the shore (like our clams); this particular shell-fish was called "Buccinum" or "Murex." Others were taken at sea, more like oysters; these were called "Purpura" or "Pelagia." "Purpura," of course, is the Latin equivalent of our word "Purple," and indicates where that particular color obtained its name.

Swinburne, in his book "Travels in the Two Sicilies" gives an interesting description of the anatomy of these little creatures, and shows how the precious dye is contained in a sort of vein, located in the central portion. By cracking the shell, this vein may be easily extracted with a hook. The veins were laid in a cistern and macerated, and after standing awhile the clear dye solution was drawn off into a lead cauldron and heated. He states: "The dye was tried by dipping locks of wool in it till they had imbibed a dark color. As the color of the Murex would not stand alone, the dyer always mixed a proportion of Purpura juice with it. They steeped the wool for five hours, then shook, dried and carded it; dipped it in again, and again, till it was saturated with the dye. The preparation requisite for staining 50 lbs. of wool, with the finest deep amethyst color, was 20 lbs. Murex to 110 lbs. of Purpura. To produce the Tyrian Purple, which resembled the color of coagulated blood, it was necessary, first to steep the wool in pure unboiled Purpura juice, and then let it lie and simmer with that of the Murex." By different mixtures of these two dyes, variations of shade were obtained according to the changes of fashion.

You have all heard the famous recipe for Hare Soup, which starts off with the instruction "First catch your hare." Just so, the rule for dyeing Tyrian Purple is incomplete without some directions for catching the Purpura, of which, as I have said, over two pounds were needed for every pound of wool to be dyed. As usual, we turn to Pliny, and are not disappointed. "Now these Purples" he wrote "are taken with small nets, and thin wrought, cast into the deepe. Within which, for a bait to bite at, there must be certain winkles and cockles, that will shut and open, and be ready to snap . . . Halfe deade they should be at first, that being new put into the sea again, and desirous to revive and live, they might gape for water; and then the Purples make at them with their pointed tongues, which they thrust out to annoy them; but the others feeling themselves pricked therewith, presently shut their shells together and bite hard. Thus the Purples for their greediness are caught and taken up, hanging by their tongues."

Pliny is outspoken in condemning the high prices which dyers charged for Tyrian Purple. Writing of the "fine double-dyed purple of Tyros" he says: "A man could not buy a pound of it for a thousand deniers" (about $150). We have heard much about the modern high cost of living, but the ancient Romans apparently were more concerned over the high cost of dyeing. No wonder that Bancroft wrote "Dyed clothes were too costly to be used by any but the rich and great, or for the service of religion, or upon extraordinary occasion."

Some one may ask, what is Tyrian Purple in scientific language? About twenty years ago, the German chemist Friedlaender secured about 12,000 specimens of the Murex Brandaris, which he believed to be the Murex of Pliny's time, and after extracting the coloring matter obtained a total yield of 1.4 grams of pure dye, which gave a reddish blue shade and proved on analysis to be one of the di-brom Indigoes; in other words, a true vat dye, closely related to Midland Vat Blue R but distinctly inferior to it in shade. Judged by modern standards this dye has no particular value, and we are forced to the conclusion that the fashionable young Romans who paid $150 per pound of wool dyed with it, to use a modern expression, were gypped.

I have already mentioned that the blue of the Tabernacle was the same as our present-day Indigo. This product is unique because not only is it probably the oldest known dye (it has been found on a garment taken from the tombs of Thebes, nearly 5000 years old) but it is still used today on a large scale. There is this difference, however; before the 20th century, Indigo was exclusively derived from plants, but about fifty years ago it was analyzed and its chemical constitution was discovered, and soon after several ways of making it synthetically were found, so that today the synthetic product has almost driven the natural dye out of the market.

The coloring matter of the Indigo plant is contained in the leaves as a secretion or juice. We have no exact knowledge of the method employed in ancient times for extracting the dye from the plant, or for applying it in dyeing; but it is pretty certain that all the old-time dyers used modifications of what is commonly known as the "fermentation vat," which depends for its operation on two principles, as most of you already know: first, that Indigo, which is normally insoluble in water, is readily converted by reducing agents into a soluble yellow substance, capable of being absorbed from a water solution by cotton, wool and silk, and later re-oxidized by the air to the original insoluble blue state; and second, that this reduction of Indigo to the soluble stage can easily be brought about by a process of fermentation, in which hydrogen gas is liberated. Many kinds of fermentable materials have been used for this purpose at different times. A typical fermentation vat, about 1840 model) is described by Berthollet in his "Elements of the Art of Dyeing." A conical-shaped copper boiler was suspended by its brim over a fire; in it the necessary quantities of bran, madder, wood ashes and water were boiled together for a given period of time. The old dyers had an ingenious method for measuring the time allotted for this operation: the workman was instructed to let the pot boil "three or four Paternosters"; in other words, he recited

the Lord's Prayer three or four times while stirring the mixture, thus ensuring adequate cooking and incidentally aiding the cause of religion. When the last Amen had been pronounced, the contents of the pot were transferred to the vat proper, where the Indigo was added and the whole mass was stirred at intervals over a period of two days. Gradually the bran and madder fermented, and the Indigo changed slowly to green and finally to yellow, if the reduction went far enough. The surface of the vat was always covered with a thick coppery scum, consisting of oxidized indigo; the dyer would brush this aside and examine the clear liquor beneath, to determine its condition. *If all was well*, a stout net was let down into the vat, and the wool was thrown in and stirred around with a pole; the net prevented it from sinking to the bottom and becoming contaminated with the thick sediment. After awhile the wool was removed from the vat by hauling up the net, and exposed to the air, to oxidize it. Then it was "dipped" again, and this was kept up until the shade was dark enough.

Sometimes all was *not* well; for a fermentation Indigo vat is as changeable as a woman; even a thunder-storm has been known to upset it; it is yellowish one moment, with a rather sweetish odor; that's when it is right; then without warning it turns black, with a strong pungent smell, and dyes only a dirty gray; that's when it has too much alkali; or perhaps it changes to a russet color, with a disagreeable fetid odor; that's when the fermentation has gone too far. From all of this it must be apparent that the successful Indigo dyer of the past must have possessed not only an experienced eye but an educated nose. It is evident that the odor emanating from an Indigo vat was not exactly fragrant, for Hannay states that in the reign of Elizabeth the smell issuing from the London dyehouses so offended the Queen's nostrils that for a time the dyeing of Indigo was forbidden by law. The Indigo dyer had other troubles, too; both in England and in Saxony there was a native plant called Woad containing the same blue dye as Indigo but of inferior quality. To protect the native product from foreign competition, the authorities in Saxony in 1577 absolutely prohibited the use of Indigo, describing it as a "pernicious, deceitful and corrosive dye," or as they called it, "corroding devil." This of course was nothing but protectionist propaganda, as Indigo was no more harmful than Woad. England passed a similar law, and it was many years before the ban was removed.

Scarlet, the last of the "big three" dyes of the Mosaic period, was produced with Kermes, a coloring matter obtained from an insect, as already described. Glen gives the following formula for dyeing worsted with it: "The material is first boiled for half an hour with bran in water, and then for two hours in a bath containing one-fifth of Roman alum and one-fifth of tartar, to which some sour water has been added. It is then taken out and laid in a linen bag for some days in a cool place, and is then dyed." He states that to obtain a full shade it was sometimes necessary to use as much Kermes as wool. Apparently Kermes would be classified as a mordant dye.

Kermes dyeing is now extinct; it was superseded in the sixteenth century by another similar but better product, Cochineal, a native of America. But in its prime it was highly esteemed, and Pliny refers to the "Royal Scarlet, reserved for princes only and great Captains to wear in their rich mantles of estate and coats of arms." It is curious to note that for many centuries the dye was supposed to be of vegetable origin, because the insect frequented a certain species of oak, and was mistaken for the fruit of the tree. Even Pliny referred to it as "graine."

Another ancient coloring matter which has survived the passing of the centuries is Madder, obtained from the root of a plant grown in Turkey and later in Holland. It is known to have been used by the Egyptians, and Pliny refers to it also, though in regard to its application he says "Little is known to any but the sordid and avaricious, and this because of the huge profits which are derived from it." The point of particular interest which appeals to the average housewife is the fact that Madder is, or rather was, used in the production of the old-fashioned Turkey-red now almost obsolete in this country, but still considered the standard for bright, fast reds on cotton. It is also one of the oldest known dyeing processes, and some historians believe that the scarlet thread mentioned in the 38th Chapter of Genesis was dyed in this manner. Despite its name, Turkey-red was first produced in India.

The process of dyeing Turkey-red is easily the longest dyeing operation on record, and maybe some of you would be interested in hearing about it. I recently came across a detailed description of an old formula used in Persia, evidently dating from a period when time was no object and odors of no consequence. The production of this tinctorial triumph was carried out in at least thirteen separate stages, somewhat as follows: The cloth or yarn was first boiled for 24 hours in a lye made from wood ashes, and dried. It was then oiled with a savory mixture of fish oil, cow dung and more lye; the goods were then removed, piled up, covered with straw and left for five or six days, and finally dried in the sun. Next, this last process was repeated, but with the cow-dung omitted (this must have been an oversight). The material was now washed twice with more lye, drying after each operation. Then followed one more impregnation with fish oil, another rinse in lye, and a good thorough wash in clear warm water. Now they were ready for the actual mordanting; first came a decoction of sumach and nutgalls, in which the goods were left, probably for several hours; then they were put into a solution of alum for a considerable time, possibly 24 hours, and dried. Dyeing took place next; the dye-bath contained madder and ox-blood. The goods were entered hand-warm and left for 24 to 36 hours with steady handling, then washed and dried. Finally they were brightened by boiling in lye in a covered kettle for 24 to 36 hours, then washed

and dried for the last time. The CIO and the NRA would probably have objected to some of these operations, and our modern customers who insist on two weeks deliveries would have gone crazy. In passing, it is interesting to note that the madder of the past and the Alizarin of the present are chemically identical.

One of the old-time dyes, which the Egyptians used to dye their mummy cloths yellow, was Safflower. This plant, also known as Saffron, contains two coloring matters, a yellow and a red. The yellow is easily extracted with water, and is so terribly fugitive that is is a wonder that it survived the passing of the centuries even though buried with the mummies. It is, however, still doing duty, we are told, in certain sections of India for dyeing pure silk fabrics used in the great popular festivals. The red color from Safflower was also used on silk, producing a brilliant but fugitive scarlet. According to Hannay, it was at one time used in England, believe it or not, to dye the Governmental Red Tape. Cagliostro states that the Greeks used it as a color for royalty, and that in Ireland for centuries the king's mantle was dyed with it.

Another yellow dye was Weld, also derived from a plant, and much used by the Romans, along with alum and copper. Pliny wrote of Weld: "I find that it is a most ancient color and highly reputed of in old rhyme; for the wedding veil which the bride wore on her marrying day was all of yellow, and women only were permitted to use them, which might well be the cause that this color is not reckoned among those that be common as well to men as women." Pliny should have seen some of our modern sports clothing.

Black was dyed in several different ways in the early days; first probably with a decoction of iron dissolved in vinegar or sour bran water, with which the cloth was saturated and allowed to lie around awhile, to oxidize the iron; then it was treated with tannic acid obtained from nutgalls, thus producing tannate of iron, which is not a bad black if you get enough of it on the fiber. Ordinary writing ink still contains this black as one of its ingredients. Another old method of making a black was by dyeing a heavy shade of Indigo and "topping" with Madder. But the favorite way, after the discovery of America, was by the use of Logwood, a brownish dye obtained from the wood of a large tree with a still larger name, growing in the West Indies and Central America. Pellew states that it was discovered and used by the Spaniards early in the sixteenth century, and soon after was introduced into England, but was violently opposed at first because the blacks obtained with it were much more fugitive than the "woaded and maddered" blacks already in use. In fact, during Elizabeth's reign a law was enacted, prohibiting the use of logwood in the dyeing of cloth "as a practice false and deceitful," and directing all logwood found to be burned. In spite of this, most dyers continued to use it under a different name. It seems quite probable that there were bootleggers in those days, even as now.

One of the most primitive dyes was Iron Buff, or plain ordinary iron rust. Some pioneer dyer discovered away back that when he dipped cloth into a spring containing soluble iron salts, and exposed it to the air, a yellowish color was developed. This sort of dye was used in earliest times, for we find it in mummy cloths 4500 years old. As might be expected, it is very permanent, and even today it finds large use as a color for tent cloth; and those who have visited the Mediterranean will remember the bright reddish sails on the fishing boats, which are dyed in like manner. Iron Buff is, or rather, was the foundation for military khaki, which for many reasons deserves a whole chapter of its own. Khaki was not one of the "dyes of our ancestors," unless one happens to be descended from a Hindoo, but at the risk of exceeding the time limit I would like to say a word about its origin and evolution.

When the English first undertook the conquest of India, nearly a century ago, military etiquette required a certain type of uniform for all British troops, no matter in what part of the world they might be fighting. You know what the uniform was like, with its scarlet tunic, black hat, pipe-clayed belt, and so on; just like soldiers in a comic opera, or as Lord Wolseley once remarked, like a monkey on a hand organ. The troops were much handicapped, fighting in a tropical climate in this impossible costume, and could not help admiring the light, comfortable cotton garments of the native soldiers, which had been stained a sort of dust-color with some kind of a mineral dye; far more serviceable than the British uniforms, but what is still more important, much less conspicuous on the field of battle. In other words, man was just beginning to discover what birds and animals have always known: the principle of protective coloring, which guards our wild life from destruction by their natural enemies. Having once made this discovery, the British were quick to take advantage of it. The dye used by the natives, which they called "khaki" or dust-colored, was employed at first, and gave trouble because it was not at all fast to washing, so that the uniforms grew constantly lighter in shade; but khaki as a military principle made a great hit with the army, and soon it was being used not only on uniforms but on water bottles, haversacks, helmets, gun carriages, every conceivable article of military equipment. Even the white horses of the famous Scots Greys, according to Pellew, were treated with a solution of permanganate of potash, which converted them in a few days into a soft, quiet shade of brown. Shortly thereafter a process was devised in England for producing a permanent shade of khaki on the uniform cloth with a combination of oxides of iron and chromium; in other words, a sort of modified iron rust. This is the khaki which our boys wore through the Spanish-American war, and which is still, possibly, the official khaki of the British army.

To revert to the ancestral dyes once more: In 1669 occurred an event which had a marked effect on the whole

dyeing industry. Colbert, the Minister of Finance in France, undertook to improve the state of the dyeing industry in that country, and instructed a man named d'Albo to compile a code of regulations for dyers, which was published in Paris in 1672, under the title "General Instructions for the Dyeing of Wool in All Colors, and for the Cultivation of the Materials which are Employed Therein." The most conspicuous feature of these regulations was the division of all the dyers into two classes, "Dyers of the Great Dye" and "Dyers of the Little Dye," or to use modern terms, dyers of fast colors and dyers of fugitive colors. All dyes were likewise separated into two classes, fast and not fast, and the instructions specified what kind of dyes should be used on every kind of wool goods. Dyers of the "great dye" were forbidden to use, or even to own, the "little dye," and vice versa. One sentence from the Regulations I thoroughly approve of, and would like to see posted in large letters in every dyehouse everywhere: "All visible objects are distinguished or rendered desirable by their colors, which must be not only beautiful, to give commercial currency to the stuffs, but also good, that their durability be equal to that of the fabrics to which they are applied."

Now I must mention an important event which occurred in 1856, and which completely revolutionized the art of dyeing; namely, the discovery of the first coal-tar dye by Perkin, a young English chemistry student, who with more enthusiasm than judgment was trying to produce quinine in the laboratory by oxidizing aniline. Finding to his surprise that the result of his labors had a strange purple color, which was contrary to Hoyle, he had the good sense to abandon the quest of quinine and investigate the unknown substance, and succeeded in isolating a totally new dye which he named "Mauve"; a dye, by the way, which is said to have been used afterwards by the British on one of their postage stamps, but has long since disappeared from the market. From this small beginning grew the colossal modern dye industry, which has almost driven the natural dyes completely off the map. But we are getting away from the ancestral dyes, and my time is up.

Industrial Plant Design:

Raw Stock Dyeing Machine*

A. L. THOMAS†

THE process of the dyeing of cloth and the problem of the design and installation of machinery for this specific purpose is a problem of major interest to the textile industry. The process in itself is relatively simple, but the variations of results therefrom has been one continual source of trouble and has caused more "gray hairs" to the managers of that department than perhaps any other feature of the entire textile field. The development of the process from the first beginnings is a most nteresting study.

From records of the ancient peoples, we learn that the art of imparting any color to and fixing it upon wool, silk, cotton, linen, skins, etc., with sufficient tenacity not to be removed by water or ordinary usage has been practiced from most ancient times, long before any correct views were known of the nature of the changes, and is still practiced by many who as yet, know very little about the chemical science involved therein. History reveals that garments of deep color were set apart as marks of distinction. Calico printing in the time of Pliny indicates no small degree of tinctorial skill, and in 1500 B.C. the Tyrian purple was set aside by the King of Phoenicia as a badge of royalty. Our very latest news reels "in natural color" exploited to the fullest the great array of special costumes of Royal Purple and Gold at the crowning of the new King and Queen of England. A most interesting account of the development of the dyes is found in an old dictionary of Arts, Manufacturing and Mines, by Robert Hunt, F.R.S., Vol. II (Longmans, Green).

The relations of the process of dyeing with the elements of chemistry and the reactions obtained constitute the theory of the art. Intelligent handling of the process requires a knowledge of facts pertaining to:

1. The nature and properties of the elements which are brought together;
2. Condition and circumstances in which these materials are brought together facilitating or retarding chemical action;
3. The phenomenon which appears during this action;
4. Properties of the colored combinations produced;
5. Proper arrangement of the apparatus, control of the color, the pressure, the duration of treatment, etc.

It is not the purpose of this paper to explain the scientific process, but rather to call attention to the problems involved therein, and to suggest some improvements that might be put into more general use. The chemist must set out the facts and outline the process; he now has

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available, complete flow-sheets for every industrial process. These must be analyzed and clearly explained to the operating employees. The engineer must study the flow-sheet and make up a continuous process layout. He must find ready built machinery, or design and have constructed new machinery for each stage of manufacture. Modern Catalogue Studies will help the engineer keep up-to-date on new and improved machinery.

The chemist and the engineer must check the final plans and inspect the construction and installation of machinery regularly to see that it is properly spaced, conveniently and adequately connected, and then adjusted for precision of operation and the most efficient handling of the materials. Thus we see that the scientist and the engineer must work together to bring about the best possible results for the management of the plant.

Shortly after the great financial crash and resulting industrial stagnation of 1929, a branch of the U. S. Government made a study of the causes as well as of the effects of business failures. Some startling facts were pictured to various industrial groups concerned therein. Hundreds of manufacturing plants had closed from a lack of scientific guidance. Thousands of employees were thrown out of work, and millions of dollars of investment of the people were lost forever. The survey revealed 85 per cent of industry operating without adequate scientific guidance; 67 per cent of machinery inefficient, and most machine tools in need of repairs; and 45 per cent of equipment practically obsolete.

After thorough consideration of the problem, the President set up the National Resources Committee. The objective: "To give lasting substance and direction to planning and extending the wise use of human and natural resources." The P. W. A. was set up to coordinate and promote adequate planning in all state and federal projects. The cooperation of the agencies of research and of industrial planning with proper refinancing, has restored countless numbers of formerly idle or deserted factories to useful and profitable industry. The three "big, bad wolves" were found to be: ignorance, selfishness, and bad judgment. There is ever lacking a real knowledge of *facts*. Future action must be based upon thorough scientific research and good engineering practice. Science will accept only facts which can be determined as being *true*. The engineer must accept responsibility for the proper utilization of the facts as determined by science.

It was found that the untrained industrial managers of yesterday attempted to keep pace with progress by imitating the scientist. Without adequate research and expert technical advice, the results were disastrous for most of them. "A little learning is a dangerous thing." Knowing how to start the car is exceedingly dangerous unless one also knows how to guide and to stop it. Laymen had learned to question and to imitate scientific effort, but had not learned how to build intelligently. The greater the number of *facts*, the more difficult it is for the average person to form correct judgment of what the situation really means. It is the specific function of the engineer to arrange and plan for the wise use of the assembled facts as determined by the scientist. The most progressive industry of today has through scientific research and competent engineering service departments employed continuously in developing better methods and incorporating the new processes promptly in the plant layout.

This particular group of textile managers and salesmen may not be specially interested in the scientific set-up, but, you might be interested in seeing how this idea has been put into practical use. Take the old raw-stock dye machine as an example:

The process of dyeing raw-stock is more or less familiar to all. The arrangement of the dye-tank, the pump, valves, etc., has been left as it was found in the dusty corner of the dye department some thirty years or more. Notwithstanding the knowledge of the many improvements in machinery and of the better scientific arrangement for more accurate control of the process, the old set-up is allowed to remain 'in status quo" and the operatives muddle along as best they can without hope of improving the quality of their work.

This equipment found in many mills in our territory is sadly in need of repairs, remodeling, or possibly renewing throughout. The arrangement of the apparatus in one plant was very poor, and after a little study and planning of a new layout, it was found that the process could be greatly improved by changing position of certain equipment, and setting all valves of control within easy reach of the operator. The new layout of the same old machinery, with the correction in location and the addition of a few pipes and valves should increase the efficiency of the apparatus materially, and insure prompt and thorough control at every stage of the process.

While I do not feel that I have brought anything new to your attention, I do hope that you will give a thought to that old equipment, and when you get around to remodeling, get the facts regarding the latest designs of the process, and call in a reliable consulting engineer to design the location and arrangement, and insure the very best installation of new machinery, "for the good of us all."

Control of Variables in Rawstock Dyeing*

J. H. O'NEILL†

TO the average individual who is not acquainted with dyeing and manufacturing problems and variables, it is hard to explain why he can so seldom duplicate in the same fabric the exact shade of material he bought six months or a year ago. Certainly no explanation would make a prospective purchaser satisfied to accept two shades in the same garment and yet we know that in the making of certain fabrics, even slight variations are magnified in processing and cause distinct shades in the finished cloth.

Since these shades present a very real problem to the cutters, it is becoming increasingly difficult to dispose of such goods, and the variables responsible for them must be controlled more closely than ever before.

Those of you who are responsible for the control of shades in rawstock dyeing no doubt have problems peculiar to your own plants, but there are also a great many problems that we have in common and a discussion of them would probably be of benefit to all of us.

The first variable encountered is in the cotton itself, coming as it does to the average mill in a number of grades, varying shades of white and sometimes tinged. This, of course, can be controlled by adopting and maintaining a uniform blend of from twenty to forty or more selected bales, which are usually run through an opener for the preliminary cleaning and blending before baling for the dyehouse. Samples of each mix should be taken and compared to avoid the risk of trouble with light shades.

These bales should be reweighed just before loading in the machines and the tags, with the bale and machine numbers, the sum of the two bales, allowance made for bagging and ties and the amount added or deducted, sent to the office to be checked for accuracy. Before making this checkup a matter of routine, we traced heavy and light dyeings to mistakes in weighing and calculation of the amount loaded.

Our dyeing is done entirely in the Morton single circulating pressure type machine with the liquor flowing through a perforated plate attached to the lid, down through the load and the perforated false bottom, back into the circulating tank where the belt-driven centrifugal pump picks it up and circulates it. It is also equipped in our case, and I believe in most cases, with air connections to a compressor for aeration of the stock.

My remarks will be confined to this machine since machine variables are somewhat limited and similar in character. In bleaching out the machine between colors, we use chloride of lime, and in tracing down the tendency of our first batch on a continuous run to check up light, we found that some of the bleach liquor was being left in the convex shaped bottom of the machine. To overcome this we made it standard practice to remove the false bottom and clean out thoroughly, resulting in better matches of a large batch with a single batch, as is often necessary to complete an order. The later Morton machines have a concave bottom with a drain in the center, and do not require this extra operation.

The method of loading which has worked out best for us is to pack the cotton in thin layers around the outside of the machine with the highest and most tightly packed point where the liquor enters from the top, leaving a small hole in the center to aid circulation.

We have traced uneven dyeings in these machines to insufficient pressure caused by slack belts and pumps in need of overhauling, to air pockets caused from a leaking air valve, to careless loading of the stock, and in the case of a vat color, to using too much alkali in the springing bath. We have also had trouble with leaking drain valves causing a loss of dyestuff, at first negligible but gradually increasing, with a natural tendency of the batches coming up lighter, and unevenly dyed where the loss of head in the circulating tank is sufficient to affect the pressure. Since the shade change is gradual, it is easily overlooked and therefore dangerous. Our machine operator is instructed to note and report any loss of volume in the circulating tank during the course of each dyeing. Watching the pressure gauge, checking temperatures, and making changes are his responsibility, and a copy of the running formula for each machine must be kept constantly before him.

Standards are very essential in the weighing and boiling up of drugs. Cleanliness of equipment, such as scoops, buckets, balance pans, etc., keeping all dyestuff drums covered while weighing to avoid dusting, weighing according to the standard methods used in the plant, all these must be drilled into the drug weigher until they become second nature to him. It is also advisable to use a measuring stick in the boil-up tanks, marking the exact volume of liquor required when the dyestuff reaches the boil, and we require all drugs to be boiled exactly five minutes.

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In cases where only a small quantity of a direct color is used this is not really necessary, but the adoption of one simple standard for all colors reduces the chance of error. So far as it is practical we apply this same principle to the running formula of direct and sulfur colors in medium and heavy shades.

Of course, light dyeings and those which must be after-treated call for special instructions as to temperatures and salting, but to a certain extent these shades, too, can be grouped and standardized.

Those shades which depend on aeration of the stock for their full development, such as the leuco dyeing sulfur blues, are very difficult to control. Any variation in air pressure or in the length of time it is applied gives a greener or redder cast to the shade, and where the blue is used in combination with a black, it is hard to place the responsibility for an off-shade. Certainly, a dyehouse having any quantity of this type shade should have a constant supply of air and the pressure should be checked frequently during the aeration period.

Variations in standard of dyestuffs and chemicals will creep in from time to time regardless of how reliable the sources of supply. The ideal method of avoiding trouble in this respect would be to have each lot and each barrel checked in the laboratory before using, but in the average mill the laboratory men are kept busy on color matching and necessary routine testing. Carload shipments of chemicals are of course checked, the analysis entered in the log, and samples retained for reference. In the dyehouse the drug weigher takes a sample of each new lot of dyestuff as it is opened, showing the lot and barrel numbers, and he uses from this lot until it is finished. In the case of an off-shade for which there is no apparent explanation, this sample is immediately checked against the previous lot and the laboratory standard. Since variations in standard of dyestuffs are rare, this usually serves merely as the first step in a process of elimination to determine the real cause.

The process of elimination is the real test of how well the system of control is working, for if the regular check-up of machines and methods is carried out, the watchful foreman can mentally eliminate most of the possible variables and narrow the investigation down to one or two factors, or where the human element is responsible he can pretty well judge how and where. The nature of the off-shade is often a key as to who and what was responsible for it, especially on an established formula where the colors and how they act in combination and under given conditions are known to the dyer.

When a shade variation appears and keeps recurring on an established formula, every possible means of determining the cause should be exhausted before changing the formula. Where the dyer changes his formula whenever his shade fails to check, his organization gets out of control, and in a short time he cannot depend on the accuracy of his formulae or the way in which they are being followed.

Given a well trained personnel, a good control system, standardized production methods and established formulae, a dyer should have plenty of time to work on those things we would all like to work on: revision of formulae, trying out new combinations to cut cost, etc., but the human element being what it is, ourselves included, variables do not stay controlled and where there are many shades and small batches of each to dye, he is in a dog fight, and like all overseers under present conditions, doomed to spend a goodly share of his time in the doghouse.

OUTING, SOUTH CENTRAL SECTION

THE Annual Summer Outing of the South Central Section was held at the Lookout Mountain Hotel, Chattanooga, Tennessee, Friday and Saturday, August 6 and 7.

The Program was officially under way Friday Afternoon when preliminaries for the horseshoe pitching tournament began. "Suds and Pretzels" were also enjoyed, by many members, in the Sunken Garden, music was furnished by the Lookout Mountain Hotel Orchestra. Following dinner many members and guests went to the Patio for the dance.

Men's and Women's games were very popular Saturday morning, with a large number of members taking part in the foot races; three legged races; and cracker-eating contests.

Golf, Skeet Shooting and Bridge were the activities Saturday Afternoon. The Golf Tournament was held at the Meadow Lake Golf and Country Club, and Skeet Shooting at the Chattanooga Rod and Gun Club.

The banquet, Saturday Evening, was well attended. Mr. A. R. Thompson of Charlotte, North Carolina, was toastmaster. "A Professor Quiz" contest was conducted, Mr. S. I. Parker answered every question and easily won. Mr. A. K. Haynes of Atlanta, Georgia, won a handsome wardrobe suitcase for the attendance prize. After the Banquet dancing was enjoyed in the Dining Room, and the Patio, of the hotel. Over 220 members and guests were registered, and the Outing was one of the most successful ever held by this Section.

LIST OF EVENTS AND WINNERS:

Golf Tournament:—Mill Men: Fletcher Kibler, Chattanooga, Tennessee. Salesmen: Frank Myers, Chattanooga, Tennessee.

Skeet Shooting:—Cliff Campbell, Cleveland, Tennessee.

Horseshoe Pitching:—Singles: W. T. Evans, Harriman, Tennessee. Doubles: Frank Cater, Chattanooga, Tennessee—J. R. Newell, Carrolton, Georgia.

Most Ringers:—Melvin Cooper, Chattanooga, Tennessee.

MURRAY B. SMITH,
Secretary.

Ed. Note: There follows a list of captions for the photos on the opposite page taken at the Outing.

1. Committee in charge of outing. Sitting left to right: William J. Kelly, Jr., Chairman Publicity; Mr. Walter E. Hadley, Chairman; Mr. Robert Cowan, Arrangements; Mr. Richard Smith, Registration; Mr. Bob Covington, Chairman Golf; Mr. Fletcher Kibler, Golf. Standing left to right: Mr. Dan Rion, Golf; Mr. Murray Smith, Program; Mr. Harold Schroeder, Arrangements; Mr. W. H. Shire, Arrangements; Mr. A. T. McDowell, Registration; Mr. John L. Dabbs, Jr., Finance; Mr. C. C. Cayce, Games; Mr. Homer Whelchel, Chairman Horse Shoe Pitching.
2. Ladies Committee. Left to right: Mrs. G. W. Searell, Games; Mrs. H. O. Shuptrine, Bridge; Mrs. Fletcher Kibler, Registration; Mrs. Frank Myers, Games.
3. Lookout Mountain Hotel, Convention Headquarters.
4. Group of members of the Association and their wives attending summer outing.
5. Prizes for various events on program.
6. Robert Covington, Chairman Golf (Covington sitting). Left to right: Harold Clark, Noel White, T. R. Johnson, A. K. Haynes, M. T. Barnhill.
7. Golf Foursome. Left to right: Dick Smith, Atlanta; Vayden Shadden, Atlanta; F. R. Johnson, Chattanooga; Fletcher Kibler, Chattanooga; (winner of golf meet).
8. Contestants in three-legged race. Left to right: Fletcher Kibler and Dick Newell; C. C. Cayce and Melvin Cooper; H. E. Hattersley and Pete Gilchrist.
9. Skeet Shooting. Left to right: W. C. Campbell, H. O. Shuptrine, C. L. Glass, Frank Cater, Murray Smith, Bill Griffin.
10. Horse Shoe Pitching. Left to right: Melvin Cooper, C. C. Cayce, Homer Whelchel, Chairman; Dick Newell, Frank Cater.

LOOKOUT MOUNTAIN HOTEL

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary or the American Dyestuff Reporter any vacancies which may occur in their businesses.—H. C. Chapin, Secretary, Lowell Textile Institute, Lowell, Mass.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive.

NOTE: PERSONS WHO HAVE OBTAINED EMPLOYMENT SHOULD NOTIFY THE SECRETARY OR THE AMERICAN DYESTUFF REPORTER AT ONCE.

Prospective employers may file vacancies either with the secretary or the American Dyestuff Reporter.

A-1

Education—B.T.C., Lowell Textile Institute.

Experience—Two years as chief chemist in cotton mill. Experienced on direct, vats, naphthols, sulfur, basic and developed colors. Two years' experience in protein, fat fiber and mineral control in grains and animal feedstuffs. Age 28.

A-B-1

Education—Graduate chemist and colorist from a leading textile institute. Speaks French fluently. High standing at school. Awarded 1st prize in chemistry. Member of honor society.

Experience—Knowledge of most processes of textile manufacturing and some experience in woolen and worsted piece and stock dyeing and color matching. Presently employed in other department but wishes to get into laboratory or dyehouse.

A-B-5

Education—Graduate of the University of Lausanne, Switzerland. Doctor's degree in Chemistry. Knowledge of French and German.

Experience—Eleven years with large bleaching, dyeing, printing and finishing plant as assistant Chemist and then Chemist in charge of the Laboratory. Experience in dyeing and printing cotton and rayon fabrics; research and analytical work. Woman.

A-B-7

Education—Evening school in textile dyeing and chemistry.

Experience—Dyehouse laboratory for 2 years. Foreman dyer and finisher on hosiery for 9 years. Experience on ribbons also vat dyes on rayon and silk skeins. 2 years assistant to superintendent. Desires position either in demonstrating and sales or dyer. Age 31; married.

A-B-C-2

Education—Graduate of Lewis Institute of Engineering of Chicago and graduate of Philadelphia Textile School (Chemistry and Dyeing department).

Experience—Has had extensive experience as assistant chemist and colorist in silk printing, dyeing and finishing; also dyeing raw stock wool; and dyeing and finishing cotton and rayon. Age 30; married; references.

A-B-C-3

Education—Graduate, Chemistry and Dyeing Course, Lowell Textile Institute, 1934.

Experience—Has experience as chemist; dyer of union knit goods (cotton and woolen); experienced bleacher on both. Has handled Tube-Tex processing on cotton and rayons. Single; will go anywhere.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following: celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-4

Experience—Foreman dyer in charge of ribbon dyeing for 20 years. Experienced on silk, cotton, rayon, acetate yarn. Age 41; will go anywhere.

B-5

Education—High School and Textile School Graduate.

Experience—Twelve years overseer of dyeing on directs, vats, naphthols, sulfur, basic and developed colors. Also experienced bleacher. Age 40; married; references.

B-6

Education—Textile School Graduate.

Experience—Former instructor in chemistry and dyeing. Twelve years' experience as overseer of dyeing of vats, naphthols, developed, indigosols, sulfur and direct colors on piece goods. Age 35; excellent references.

B-F-1

Experience—As executive had charge of the dyeing of ribbons and piece goods for 6 years; spun silk yarn, fast and resisted dyeing for 8 years; hosiery for 12 years. Has been quite successful in all three of these mills. Age 50 married. Will go anywhere.

F-1

Education—Graduate of School of Textiles, Saxony (1925). Graduate of School of Commerce of University of Berlin (1928).

Experience—Worked in various departments of textile mills as worker, later as a supervisor. Familiar with the production, calculation and management of manufacturing. Thirty years old; unmarried.

Fractionation and Composition of

Sulfonated Oils*

RALPH HART

A rapid and reliable procedure is given for the quantitative fractionation or separation of the various fatty components contained in sulfonated saponifiable oils. Data obtained as a result of the application of this method to samples of commercial sulfonated olive and castor oils indicate that the reaction between concentrated sulfuric acid and a fatty glyceride is comparatively simple and that no polymers, or very little, are formed. These findings are contrary to the generally accepted view of the sulfonation reaction. The probable composition of each of the fractions separated is given and the probable course of the sulfonation reaction is represented by an equation.

IN the manufacture of the ordinary commercial grade of sulfonated oil, made from such oils as castor, olive, neat's-foot, etc., the raw oil is usually treated with about 25 per cent of strong sulfuric acid. In the case of glycerides whose fatty acids have either one double bond or one hydroxyl group, this quantity of acid corresponds approximately to 3 moles of sulfuric acid to 4 of the fatty acids. Actual sulfonation, however, occurs only to the extent of 25 to 30 per cent instead of the theoretical yield of about 75 per cent; hence, the ordinary sulfonated oil is a mixture of sulfonated fat, unchanged glycerides, free fatty acids, and polymerized oils. Because of the complexity of the mixture and of troublesome emulsions formed during extractions with solvents, very little headway has heretofore been made in developing a method to fractionate or separate the different components existing in a sulfonated oil.

There seems to be a feeling among users of sulfonated oils, particularly among leather chemists, that a knowledge of the structural composition of a sulfonated oil might help to explain certain variations and nonuniformity sometimes noted in materials treated with such products. This information would also be of great value in determining the nature of the raw oil or oils used in the process and whether or not the sulfonated product contains any admixture of raw oil. Attempts have therefore been made recently to develop methods for fractionating sulfonated oils. The American Leather Chemists' Association[3, 6] had appointed a committee, which left the matter pending, to investigate the determination of neutral fat in sulfonated oils. Winokuti, Igarasi, and Yagi[10] outlined a procedure for determining neutral fat, fatty acids, and sulfo oil, which is not supported by sufficient quantitative data, and which yields imperfect separations of the components as well as troublesome emulsions during extractions.

Schindler Method

The best known of the fractionation methods is that of Schindler[1, 7, 8]. The writer finds the method involved, tedious, uncertain, and inexact. Burton and Robertshaw[2] state that the Schindler method, although valuable, is very complicated and gives incomplete separation of the fractions, and that when the sulfated oil contains a high proportion of water or added neutral saponifiable and/or unsaponifiable oil, the fractionation does not yield quantitative results. Some changes in the Schindler method proposed by Theis and Graham[9] seem to have improved it very little.

New Method

A procedure is here outlined which separates quantitatively (A) sulfo oil, (B) fatty acids, and (C) neutral fat. The method is not affected by admixtures of saponifiable oils, mineral oils, or water, and is applicable to oils of the type of ricinoleic acid as well as oleic acid. The method is accurate and simple, and check results are easily obtainable. A complete fractionation in duplicate may be carried out in about 4 hours. The analysis of the various fractions has also led to a theory of the composition of the sulfo oil and of the chemical reactions that may take place between the acid and the glycerides during sulfonation.

During this investigation it was found that no emulsions are formed and that sharp separations occur when a somewhat concentrated solution of sulfonated oil in water, on either the acid or neutral side, is extracted with ethyl ether or petroleum ether. The extractions may be successively repeated any number of times with the same result, but any attempt to wash the solvent layer with water results in unsatisfactory separations. The ether layer, however, is contaminated with a variable but small amount of sulfo oil—the quantity depending upon the efficiency of the extractions and the ratio of solvent to solution. Every effort made to remove the sulfonated oil from the ether layer proved unsuccessful. Although the emulsions formed upon washing with water were easily broken by small quantities of electrolytes, such as sodium sulfate, the sulfonated oil was found to be redissolved in the ether layer.

By the proper proportioning of the solvent and solution, all the neutral fat and the fatty acids may be quantitatively separated from the sulfo oil by extraction with

*Ind. and Eng. Chemistry.

ether. The ether extract, containing the neutral fat and the fatty acids (and some sulfo oil), is then neutralized and the neutral oil is extracted in a similar manner. The water layer from the ether extraction contains the sulfo oil, substantially free from all unsulfonated fractions. By applying a correction factor for the sulfo-oil contaminant in the ether layer, the neutral fat, fatty acids, and sulfo oil may be quantitatively estimated.

Procedure

FRACTION A, SULFO OIL. Dissolve 10 grams of the sample in 25 cc. of water in a 250-cc. separatory funnel and add 50 cc. of ethyl ether, 5 drops of methyl orange indicator (0.1 per cent solution), and 0.5 *N* sulfuric acid until the lower layer after vigorous shaking and settling is faintly pink. Shake the mixture vigorously for about 1 minute and allow the layers to separate well. Excess water used in dissolving the sample often results in emulsions or the formation of gels, which, however, may be overcome by the addition of 5 to 15 cc. of alcohol. A moderate turbidity in the water layer after this extraction may be disregarded. Separate the two layers and again extract the water layer—which contains the sulfo oil—with two 25-cc. portions of ether.

Add to the water layer in the separatory funnel 10 grams of solid sodium chloride, 5 drops of phenolphthalein solution (1.0 per cent), and 50 cc. of ether, and titrate with 0.5 *N* sodium hydroxide solution until the lower layer after vigorous shaking and settling is faintly pink. Now add 5 drops of methyl orange and sufficient 0.5 *N* sulfuric acid with vigorous shaking until the lower layer is again faintly pink. Add enough dry salt until a slight excess is present. After settling, discard the lower or salt layer, evaporate the ether from the upper layer, and determine the organically combined sulfuric anhydride and the fatty matter in the residue in the usual way—the former preferably by the acid-titration method[4]. The ratio of fatty matter to combined sulfuric anhydride gives the correction factor to be used in determining the sulfo oil found in the other fractions. The amount thus determined is ultimately added to fraction A.

FRACTION B, FREE FATTY ACIDS. To the combined ether layers from fraction A, containing the free fatty acids and the neutral fat, add 25 cc. of a concentrated solution of sodium chloride, 5 drops of phenolphthalein indicator, and 10 cc. of alcohol, and carefully neutralize the free fatty acids with 0.5 *N* sodium hydroxide solution with vigorous shaking until the lower layer is faintly pink. Add sufficient dry salt until there is a slight excess present, and after shaking well and settling, discard the lower layer. Shake the ether layer vigorously with 50 cc. of water, settle and separate the layers, and extract the water layer with two 25-cc. portions of ether.

Add to the water layer containing the neutralized fatty acid, 50 cc. of ethyl ether, 10 grams of solid sodium chloride, and 5 drops of methyl orange solution, and titrate with 0.5 *N* sulfuric acid with vigorous shaking until the lower layer is faintly pink. Add a slight excess of dry salt, allow the layers to separate completely after shaking, discard the water layer, evaporate the ether in the upper layer, and determine the combined sulfuric anhydride and fatty matter in the residue in the usual manner. In determining the combined sulfuric anhydride in this fraction as well as in the following, boil with the acid for several hours and agitate frequently, to make sure of complete decomposition. Correct for the presence of sulfo oil by deducting the product of the combined sulfuric anhydride contained in this fraction and the correction factor determined in fraction A.

FRACTION C, NEUTRAL FAT. Add 25 cc. of saturated salt solution and 5 drops of phenolphthalein solution to the ether layer from fraction B, containing the neutral fat, and neutralize the free fatty acids, if any, with 0.5 *N* sodium hydroxide solution with vigorous shaking until the

TABLE I

Fractional Analysis of Samples of Sulfonated Olive and Castor Oils

	Sulfonated Olive Oil			*Sulfonated Castor Oil*		
	I %	II %	Av. %	I %	II %	Av. %
Fraction A, sulfo oil						
Fatty matter, uncorrected	16.8	16.5	16.7	19.4	18.9	19.2
Combined SO_3	3.33	3.39	3.36	3.98	4.01	4.00
Correction factor (fatty matter/combined SO_3)	....	....	4.97	....	....	4.80
Correction for sulfo oil in fraction B.	....	....	3.6	....	....	2.0
Correction for sulfo oil in fraction C.	....	....	0.9	....	....	....
Total correction for sulfo oil	....	....	4.5	....	....	2.0
Fatty matter, corrected	....	....	21.2	....	....	21.2
Fraction B, free fatty acids						
Fatty matter, uncorrected	24.5	25.3	24.9	28.8	27.6	28.2
Combined SO_3	0.70	0.74	0.72	0.45	0.37	0.41
Correction for sulfo oil	....	....	3.6	....	....	2.0
Fatty matter, corrected	....	....	21.3	....	....	26.2
Fraction C, neutral fat						
Fatty matter, uncorrected	22.3	21.8	22.1	11.7	12.7	12.2
Combined SO_3	0.20	0.16	0.18	....	Trace	....
Correction for sulfo oil	....	....	0.9	....	....	....
Fatty matter, corrected	....	....	21.2	....	....	12.2
Totals						
Fatty matter found	....	....	63.7	....	....	59.6
Fatty matter theoretical	....	....	63.2	....	....	60.2
Combined SO_3 found	....	....	4.26	....	....	4.40
Combined SO_3 theoretical	....	....	4.40	....	....	4.52

lower layer is faintly pink. Now add 5 drops of methyl orange indicator and titrate with 0.5 *N* sulfuric acid, shaking vigorously until the lower layer is again faintly pink. Add a slight excess of salt, discard the lower layer after settling, evaporate the ether from the upper layer, and determine the combined sulfuric anhydride and fatty matter in the residue as outlined above. Correct for the presence of sulfo oil as for fraction B. For greater accuracy, the free and combined fatty acids as soap contained in this fraction, which is usually very small, may be calculated from the acid titration, and the result deducted from this fraction and added to fraction B.

Experimental

Samples of sulfonated olive oil and sulfonated castor oils of approximately the same concentration in fatty matter were fractionated by this method and the results, based on the weight of the original samples, are given in Table I. Under "totals" at the end of the table, the fatty matter and combined sulfuric anhydride are compared with the results obtained by a direct analysis of the original samples, which results are considered to be the correct or theoretical values. In the sample of sulfonated olive oil the fatty matter is practically equally divided among the three fractions; in the case of the sulfonated castor oil, however, the neutral fat is only about half as much (with a corresponding larger amount of free fatty acids in fraction B), and the amount of sulfo oil is about the same as in the other sample.

Purity of Sulfo Oil in Fraction A. To determine whether or not the sulfo oil fraction was substantially free from unsulfonated fat and fatty acids, the water layer containing the sulfo oil after the regular extraction with ether was further extracted with three 100-cc. portions of the solvent, with the results shown in Table II. Because of the small quantities involved, the results for the combined sulfuric anhydride are necessarily approximate. It will be noticed that the total amount extracted is comparatively small and that successive extractions continued to extract some fatty matter, though in decreasing quantities. The ratio of fatty matter to combined sulfuric anhydride indicates that the total residue had approximately the same composition as the sulfo-oil fraction in Table I. It is therefore reasonable to assume that the latter fraction is substantially free from unsulfonated ingredients.

Purity of Free Fatty Acids in Fraction B. To determine whether or not the free fatty acids in fraction B in the case of the sulfonated olive oil contained any neutral fat, the following tests and calculations were made: The saponification value of the desulfated fatty matter of this fraction was determined and found to be 190.8. The alkali equivalent of the free fatty acids in this fraction, determined as given in the method, was found to be 34.5 mg. of potassium hydroxide per gram based on the original sample corresponding to 18.1 per cent of free fatty acids (34.5/190.8), compared with 21.1 per cent actually found. A similar result was obtained for the sample of sulfonated castor oil. While the discrepancy between the calculated fatty acids and the fatty matter found may indicate the presence of some neutral oil, the difference is small and of slight practical importance, and it is believed that a more careful analysis would bring the results into closer agreement. Furthermore, some experiments carried out with the neutral fat fraction, discussed below, indicate that all the neutral fat and unsaponifiable matter had probably been quantitatively extracted; hence, the discrepancy probably indicates some polymerization.

TABLE II

Successive Extractions of Fraction A with Ethyl Ether

Sample	*Extraction No.*	*Volume of Ether* C.	*Fatty Matter* %	*Combined*[a] SO_3 %
Sulfonated olive oil	1	100	2.2	0.50
	2	100	1.1	0.18
	3	100	0.7	0.18
	Total	300	4.0	0.86
	(Fatty matter/combined SO_3)[a]			4.65
Sulfonated castor oil	1	100	1.5	0.32
	2	100	1.2	0.23
	3	100	1.2	0.16
	Total	300	3.9	0.71
	(Fatty matter/combined SO_3)[a]			5.49

[a] Approximate.

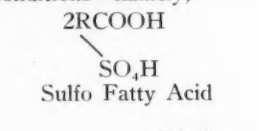
Purity of Neutral Fat in Fraction C. The free fatty acids and combined sulfuric anhydride in this fraction were found to be from a trace to 1.5 mg. of potassium hydroxide for the former and from a trace to 0.25 per cent for the latter, based on the original samples. These results indicate that the neutral fat fraction is comparatively free from either of these ingredients. To determine whether or not all of the neutral fat in the original sample is contained in this fraction, 100 parts of the sulfonated olive oil were mixed with 50 parts of neutral raw olive oil and the mixture was analyzed for neutral fat. The quantity found was 48.4 per cent, compared with the theoretical value of 47.5. In calculating the theoretical value it was assumed that the neutral fat in the original sample was equal to a 21.2 per cent in accordance with Table I. As a further check, the same oil was mixed with half its weight of mineral oil and the combined neutral fat and unsaponifiable were determined. The latter was then saponified and the mineral oil determined in the usual way. The amount recovered was 32.8 per cent, compared with the theoretical value of 33.3 per cent. The latter does not include the small amount of unsaponifiable matter naturally occurring in the oil.

Composition of Sulfonated Oils

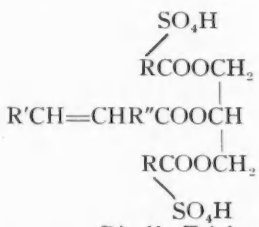
A study of the data obtained in the fractional analysis of sulfonated olive and castor oils, discussed above, has led to some very interesting speculations as to the probable composition of each of the fractions separated and also as to the reactions that may take place during the sulfonation process. It has heretofore been assumed by many investigators that the reactions are very complicated, resulting

in the formation of many involved polymers, but this investigation does not bear out these assumptions. The data obtained in this study and the conclusions arrived at follow:

SULFONATED OLIVE OIL. *Fraction A, Sulfo Oil.* The complete data obtained for the uncorrected sulfo oil in fraction A, Table I, are given in Table III. According to Jamieson[5], olive oil consists of 80 to 85 per cent of oleic acid, 4 to 7 per cent of linoleic acid, and the rest saturated fatty acids. For the purpose of this discussion it is assumed that the fatty acids in sulfonated olive oil consists entirely of the oleic acid type and also that the saponification value found for the desulfated fat, which has undoubtedly suffered some hydrolysis and condensation during the heating with mineral acid, is the same as for the fatty matter in the sulfo oil before decomposition. According to Table III, the composition of the sulfo oil corresponds approximately to 40 per cent free fatty acids; sulfonated oil, 80 per cent of maximum sulfonation; and 20 per cent unsaturated oil. In other words, out of every 5 fatty acid residues, 2 consist of free fatty acids, 4 are completely sulfonated, and 1 contains a double bond. There seems to be only one feasible composition that meets with all these conditions—namely,



Sulfo Fatty Acid



Disulfo Triglyceride

That is, the sulfo oil apparently consists of only two sulfonated compounds—namely, sulfo fatty acids and disulfo triglycerides and precisely in the proportion of 2 molecules of the former to 1 of the latter. The triglyceride may be either symmetrically or unsymmetrically sulfonated.

Fraction B, Free Fatty Acids. It has already been shown that this fraction consists almost entirely of simple free fatty acids. The desulfated fat had a cloud test of 30° C. and a solidification point 1° lower. It had an iodine value of 40.8, indicating that more than half of the unsaturated bonds in the original had been converted to hydroxyl groups, which would also serve to explain the comparatively low saponification value obtained for this fraction—namely, 190.8 instead of about 200 for olive oil fatty acids. Evidently considerable sulfonation had at first taken place but the product decomposed before it was finished.

Fraction C, Neutral Fat. The fatty matter of this fraction had the lowest solidification point—namely, 21° C.—a saponification value of 180.8, and an iodine number of 52.5. The low iodine number indicates that sulfonation followed by decomposition has taken place almost to the same extent as in the case of the free fatty acids in fraction B. However, the saponification value is 10 points lower than for fraction B—namely, 180.8 compared with 190.8; hence, the average molecular weight of the fatty matter in this fraction must be greater than for the fatty acids fraction. This indicates that at least part of the neutral fat must be in the form of glycerides, since the polymers would have a lower average molecular weight. Moreover, the extent of the difference in the saponification values indicates, assuming that the nature of the fatty acids is alike in both fractions, that the neutral fat is practically all in the form of glycerides and that practically no polymers can be present. The neutral fat, as shown below, consists probably of di- and triglycerides.

TABLE III

Analysis of Sulfo Oil in Fraction A of Sample of Sulfonated Olive Oil

	Based on Original Sample	*Based on Desulfated Fatty Matter*	
Fatty matter, %	16.7	100	
Saponification value*,†	...	190.0	
Acidity, mg. of KOH per gram	13.7	82.0	≏ 40% ± free fatty acids
Combined SO_3, %	3.26	20.1	≏ 80% ± of maximum sulfonation
Iodine No.	...	19.2	≏ 20% ± unsaturated
Cloud test, ° C.	...	38	
Solidification point, ° C.	...	33	

*Sulfonation equivalent as SO_3 = 26.3%.
†Iodine equivalent = 86.0.

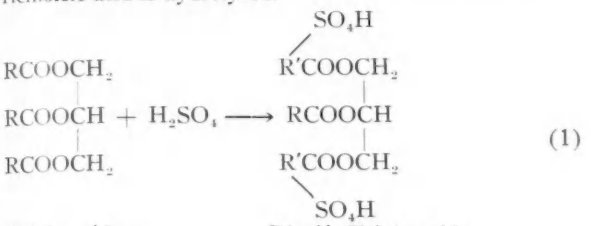
SULFONATED CASTOR OIL. The sulfo oil in fraction A of the castor oil sample had an iodine number of 77.8, indicating very little sulfonation on the double bond. The degree of sulfonation was about equal to that of the olive oil—namely, about 80 per cent—and the acidity corresponded to about 50 per cent of free fatty acids instead of 40 per cent. It is therefore assumed that the composition of this fraction is similar to that of the corresponding fraction of the olive oil sample, with the exception that the number of double bonds in the former is practically the same as for the raw castor oil.

The free fatty acids in fraction B had an iodine number of 78.9 and an acidity of 176 mg. of potassium hydroxide per gram of desulfated fat. These data indicate that the free fatty acid is nearly all pure ricinoleic acid, with the possibility of a small percentage of polymerized fatty acids. The neutral fat fraction has an iodine number of 81.8 and its composition, as in the case of the olive oil sample, is probably a mixture of di- and triglycerides of ricinoleic acid.

Reactions During Sulfonation

After a careful consideration of the data obtained in this investigation, it is suggested that the following reactions occur when neutral olive oil is treated with concentrated sulfuric acid in the usual commercial practice. Similar reactions probably hold true also for castor oil, except that a larger amount of free fatty acids is formed

because of the greater ease with which the triglyceride of ricinoleic acid is hydrolyzed.



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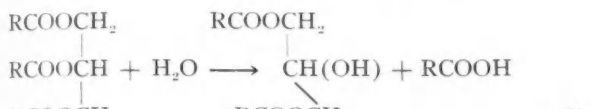
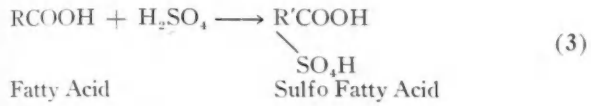


(2)



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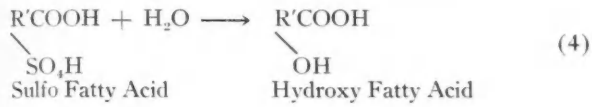
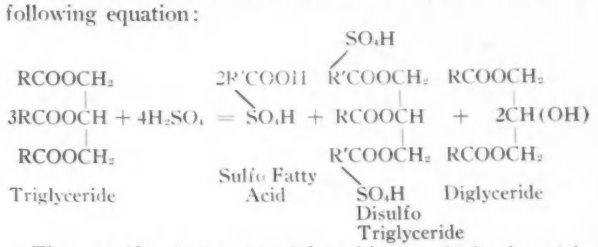


(4)

Four reactions seem to take place—namely, the triglyceride is sulfonated, yielding a disulfo triglyceride, probably symmetrically arranged; one-third of another molecule of triglyceride is hydrolyzed, yielding a diglyceride and free fatty acids; the free fatty acid is sulfonated, giving sulfo fatty acid; and finally part of the sulfonated glyceride and fatty acid is decomposed to yield the corresponding hydroxy compounds. These reactions, with the exception of the partial and total hydrolysis of the glyceride and the decomposition of the sulfo oils, may be represented by the following equation:



The unsulfated di- and triglycerides would be found in the neutral fat fraction and the sulfo fatty acid and the disulfo triglyceride would be found in the sulfo-oil fraction. The composition of the sulfo oil according to this equation corresponds to the analytical data obtained for this fraction. Hydrolysis of the disulfo triglyceride and the sulfo fatty acid would account for the low iodine numbers obtained for the neutral fat and the free fatty acids, respectively.

Acknowledgment

The writer is indebted to Morris Mytelka of this laboratory for assistance with the analytical work.

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TECHNICAL NOTES FROM FOREIGN SOURCES

Colloid-Chemistry of Modern Aftertreatments for Increasing Fastness of Substantive Dyeings to Water and Washing

Dr. A. Chwala (with A. Martina and Dr. F. Becke)—Mell. Textil-Ber. 17. 583 (1936).—Aftertreatments of a purely chemical nature, such as diazotizing and developing, afterchroming, aftercoppering, etc., to increase the fastness of substantive dyeings toward aqueous influences have been known and used for a long time (according to the patent literature, since 1887). It was apparently not so long ago, about 1923, that the Gesellschaft fuer Chemische Industrie, in Basel, brought out an entirely new method of improving the fastness of substantive dyeings. a method not to be classed as chemical in its nature; depending upon the aftertreatment of the dyeings with a new class of synthetic substances. These were, essentially, high-molecular nitrogen bases, containing a fatty acid component; one definite example of such products being oleic acid diethylamino-ethylamide. Such compounds, produced and sold under the general name of "Sapamines", formed a class properly entitled as a group of colloid-electrolytes, and under this aspect evoked a great deal of further study and development. It is of this group of aftertreatment agents that the present paper speaks particularly.

These compounds may be classified as follows:

1—colloid-electrolytes in the form of high-molecular bases with trivalent or pentavalent nitrogen.
  a—of aliphatic nature, as the typical compound cited above,
  b—of cyclic or heterocyclic nature.
2—Colloid-electrolytes in the form of high-molecular bases united with tetravalent sulfur, with pentavalent phosphorus, antimony, etc.

Some simple derivatives of some of the better known products have also been introduced into trade. Sapamine itself has been mentioned above; its hydrochloride has

been introduced under the designation "Sapamine CH", and its acetate under the brand "A". Another brand, "MS", which involves a pentavalent nitrogen, has also been introduced, as well as two others, "BCH" and "KW", about which little is known except by the manufacturers, though a rational formula for the "BCH" brand has been given. These Sapamines are products of the "Gesellschaft" in Basel; the I.G. has introduced an aliphatic high-molecular amine with trivalent nitrogen, under the name of "Solidogen B"; the Imperial Chemical Industries Ltd. have introduced an example of a high-molecular cyclic amine under the name of "Fixanol," which is prepared by heating pyridine with suitable high-molecular chlorides, bromides, phosphates, etc., such as cetyl bromide, dodecyl sulfate, etc., the products being pyridinium compounds with pentavalent nitrogen. The Sandoz firm has put upon the market "Sandofix", which is at present not understood in its chemical aspect.

Of the compounds of the second group, one example would be dimethyl-dodecyl-sulfonium chloride, or trimethyl-dodecyl-phosfonium chloride. The patent-literature relating to such compounds speaks now and then of a "salt-formation" between the dyestuffs upon the fiber, and the basic assistant in question—which seems to be mere hypothesis, in the lack of experimental evidence.

The author has carried out careful work upon the question of the true action taking place in the use of such compounds, and puts the matter plainly upon a physico-chemical basis. Though his work has been careful and exact, he states that, having been obliged to work with some substances whose purity and homogeneity is not established, or which are distinctly not pure substances, an absolute value cannot be assigned to his results—at least, till more work has been done under unimpeachable conditions.

An interesting, instructive paper.

Meeting of

American Chemical Society

Division of Cellulose Chemistry

AMONG the papers to be presented before the division of Cellulose Chemistry on September 9 at the Rochester meeting of the American Chemical Society, the following, presented in abstract, should be of interest to many AMERICAN DYESTUFF REPORTER readers.

Division of Cellulose Chemistry

E. HEUSER, *Chairman*

W. O. KENYON, *Secretary*

THURSDAY MORNING

9:00—1. Chemistry of Cellulose Derivatives — A Historical Review. R. F. Conaway, E. I. du Pont de Nemours & Company.

Cellulose derivatives constitute one of the largest and most important industries in this country as it utilized in 1936 approximately one-half billion pounds of cellulose in the form of cotton linters and wood pulp. The derivatives of cellulose may be classified broadly as esters and ethers, although other classifications based on degree of substitution and solubility characteristics are possible. The reactions involved in the preparation of cellulose derivatives are heterogeneous in nature and the resulting substituted celluloses vary greatly in their sensitivity to hydrolysis and to small changes in the equilibrium conditions of the reaction mixture. The xanthates are the most sensitive, whereas the ethers are the most resistant. These important commercial products may be considered as long cellulose chains in which the three hydroxyl groups per glucose unit are substituted to varying degrees with different groups. The chemical and physical characteristics of substituted celluloses are determined largely by the nature of the substituent groups, the degree of substitution, and the extent to which the cellulose is degraded, although other factors such as uniformity and impurities are also important. Cellulose derivatives are employed in a wide variety of industries such as rayon, plastics, lacquers, foils, adhesives, etc., and will probably continue to expand not only in these fields but into new and related industries.

9:40—2. Purification of Wood Cellulose. Fred Olsen, Western Cartridge Company, East Alton, Illinois.

The use of wood pulp instead of cotton for conversion to cellulose derivatives, especially the acetate, apparently introduces severe problems of purification. If the course of the conventional processes of bleaching and caustic treatment is extrapolated to give higher purity, so much depolymerization may occur that the strength and other properties of the finished article may be seriously reduced.

Wood cellulose has been prepared from the conifers such as spruce, western hemlock, etc., and from such deciduous woods as maple, birch, aspen, cotton-wood, etc., which compares favorably with cotton. An alpha cellulose content of 99+ per cent, pentosans of less than 1.5 per cent, and a loss in 7.14 per cent NaOH of less than 2 per cent has been obtained. At the same time the viscosity can be held, if desired, at very high levels, even higher than that of any of the available samples of purified cotton linters.

The reactivity of the purified wood cellulose is very high as indicated by the rapidity and smoothness of the acetylating reaction and the clarity and good color of the resulting acetate dopes.

The topochemical character of the reactions with cellulose make it imperative that thoroughly uniform contact of the solid phase with the liquid reactants be provided. This involves particular emphasis on permeability of the cellulose.

10:10—3. The Physical Properties of Cellulose Derivatives. H. M. Spurlin, Hercules Powder Company, Wilmington, Delaware.

The physical properties of cellulose derivatives are determined by the nature and number of the substituting groups, by their distribution along the cellulose chain, and by the molecular weight.

Tensile strength of the film is increased by long chain length and by low molecular weight per C_6 unit. Polar groups, such as OH and NO_3, increase strength and, to a greater degree, flexibility. Strength does not change as rapidly with chain length as does fold test. The latter is a good means of comparing derivatives. Uniform chain length leads to much greater flexibility and somewhat better strength.

Solubility is in all cases improved by mixed substitution. This is due to steric factors. Some content of polar groups such as NO_3 or OH is necessary for a wide range of solubility. Polar substituents also improve action of plasticizers.

Water resistance is largely a function of OH content. Some groups seem to counteract the water sensitivity due to OH groups better than others.

Light absorption of cellulose derivatives is small. Light absorbed causes degradation. Some derivatives such as the acetate are protected if light absorbing materials are added, while others such as nitrocellulose seem to become more sensitive to photodegradation.

10:50—4. Solubility, Softening and Moisture Absorption of Cellulose Ethers as a Function of Their Composition. E. J. Lorand, Hercules Experiment Station, Wilmington, Delaware.

Physical properties of the ethers, such as solubility in organic solvents, softening on heating, moisture absorption, etc., depend on the following factors:

(1) Nature of the ether group (alkyl, aralkyl, hydroxyalkyl, other substituted alkyl, etc.).

(2) Relative numbers of etherified and free hydroxyls.

(3) Chain length (viscosity) of the product.

(4) Uniformity of the product, as regards degree of substitution of the single chains.

It is shown that the influence of factor (1) may be related to the size and polarity of the substituent. In a homologous series, moisture absorption and softening point decrease with growing numbers of carbon atoms, while solubility in non-polar solvents increases.

Some of the properties show maxima or minima at certain values of (2). Maximum solubility and lowest softening temperature are reached at about the same degree of substitution. Other properties, such as moisture adsorption, seem to decrease (or increase) continually with the substitution.

Importance of uniformity and the secondary influences due to the viscosity are pointed out, and solubility in solvent mixtures is discussed.

11:20—5. The Viscosity and Optical Rotation of Cellulose Dispersed in Cuprammonium Solution. Jack Compton, Boyce Thompson Institute, Yonkers, N. Y.

The rotation and viscosity of cellulose in cuprammonium solution may be determined on high viscosity celluloses, over a wide range, by the use of cuprammonium solution containing 15 g. of copper, 250 g. of ammonia, and less than 0.5 g. of nitrous acid per liter. Making use of this reagent, it was found that the viscosity change caused by either the action of mild acids or oxidizing agents on cellulose fibers caused no change in the optical rotation of the corresponding dispersions. This result is in agreement with the work of Hess, Messmer, and Ljubitsch (Ann. *444*, 287-327 [1925]) on very low viscosity cellulose. The conclusion may thus be drawn that the rotational phenomenon of cellulose dispersed in cuprammonium solution is largely, if not entirely, dependent upon the more stable component of the cellulose fiber, i.e., the crystalline cellulose particles.

11:50—6. Homogeneity and Properties of Nitrocellulose. H. M. Spurlin, Hercules Powder Company, Wilmington, Delaware.

In order to investigate the influence of homogeneity on physical properties, a sample of half-second nitrocellulose, 12 per cent nitrogen content, was subjected to a series of three fractionations. Fractions of from one-fourth to three times the specific viscosity of the starting material were obtained. By using the Schopper fold test and stress-strain curves, films prepared from these fractions were compared with (a) regular commercial nitrocellulose and with (b) blends of high and low viscosity nitrocellulose. In each case these materials were selected so as to be of the same viscosity as the fraction under test.

The physical properties of the fractionated material, whether plasticized or unplasticized, were definitely superior to both the regular commercial and the blended samples. For example, commercial 1″ nitrocellulose gave 30 folds, a fractionated sample of the same viscosity 38 folds, and a blend of 18-25 mp. and 20″ (7,500 cp.) nitrocellulose, also of the same viscosity, only 18 folds.

Differences in the stress-strain curves were less marked, but generally in favor of the fractionated samples. Advantages of fractionation, however, were not sufficient to justify commercial use of the method.

THURSDAY AFTERNOON

2:00—7. The X-Ray Diffraction Behavior of Cellulose Derivatives: A General Review. Wayne A. Sisson, Boyce Thompson Institute, Yonkers, N. Y.

I. *Formation.* (a) Typical changes in X-ray diagram at various stages of derivative formation. (b) Interpretation of X-ray data regarding the mechanism of derivative formation.

II. *Structure.* (a) Types of amorphous and crystalline X-ray diagrams. (b) Effect of conditions of starting material and the nature and percentage of substituted groups on the type of structure formed. (c) Comparison of arrangement of substituted groups and unit cell dimensions for several derivatives. (d) Effect of plasticizers, softeners, stabilizers, ageing, mixtures, etc., on X-ray diagram.

III. *Orientation.* (a) Derivatives possessing original fiber structure. (b) Relation of derivative structure to production of orientation by stretching of fibers or drying of films.

IV. *Solution.* (a) Changes in X-ray diagram due to swelling, solution, and drying when different derivatives are treated with various organic solvents.

V. *Hydrolysis.* (a) Effect of derivative structure and nature of hydrolyzing medium on the mechanism of hydration and the type of hydrated structure obtained.

2:40—8. The Concentration of Sodium Hydroxide Necessary for the Mercerization of Different Cellulose Fibers. J. R. Katz, Brookline, Massachusetts.

Different kinds of native cellulose fibers need different concentrations of sodium hydroxide to get the same degree of mercerization.

If a bundle of native cellulose fibers is dipped at constant temperature in a series of solutions of sodium hydroxide of different concentrations (going up per ¼° C.) one finds that there is a definite concentration of the NaOH where the mercerization begins and another one at which it is complete. These two concentrations can be easily determined with the help of X-rays. Any X-ray spectrographical unit of the simplest type is sufficient to make these measurements.

In this way we find a series of highest and lowest concentration limits ranging from broom as highest to paper pulp as lowest.

Between 30° and 0° C. the lowest and highest limits of mercerization depend on the temperature according to straight lines.

An explanation of these facts is presented.

It is difficult to make quite sure which part of the fiber is the unit which changes separately from native into mercerized; because the staining methods for demonstrating the difference are not very good.

This part, however, can be made quite sure in the analogous case of the reaction between starch and sodium hydroxide. Here the same two limits—the upper and the lower one—can be found. Here, too, X-ray spectrography is a good and simple method for determining the sharp limits (highest and lowest) where the polysaccharide is changed.

With the mercerization of cellulose, we have to compare the first stage of the gelatinization of starch.

It is surprising how many cellulose problems may be greatly furthered by studying the analogous problem with starch (compare, for instance, Mrs. Farr's cellulose structures with the ones described independently in starch).

3:10—9. X-Ray Studies of Lignin. E. E. Harris, E. A. Parker, E. C. Sherrard, and G. L. Clarke, Forest Products Laboratory, Madison, Wis.

X-ray diffraction analysis of lignin and lignin materials from three different woods by two different methods gave X-ray patterns typical of the crystal lattice of organic substances with high molecular weight. The spacings in the lattice are changed by the introduction of new chemical groups as methoxyl and nitro groups, but oxidation causes very little change.

3:40—10. Observations with the Spierer Lens. L. H. Smith and Frederick F. Morehead, American Viscose Corporation, Roanoke, Va.

An attempt has been made to check the usefulness of the Spierer observation system. It is shown that the striae observed in the case of cellulose fibers are of purely optical origin. The effect of the refractive index of the mounting media has been investigated. It is shown that no pattern results unless one has refraction lines in the image due to bounding surfaces. A comparison has been made of the relative efficiency of the Spierer illumination with the darkfield illumination by means of the cardioid condensor. Photomicrographs are shown.

4:10—11. Recent Developments in Wood Hydrolysis. Eduard Färber, Heidelberg.

We do not know whether the expression "wool hydrolysis" is correct from a philological standpoint or not. What we mean is the separation of lignin and carbohydrates in a process which includes the hydrolysis of the latter. Very dilute acids and on the contrary almost or completely water-free hydro-halogenic acids have been tried for wood hydrolysis. Between these extremes lies an application of 40 per cent hydrochloric acid.

In discussing these processes one must bear in mind that beside the chemical reactions involved in them there are other features which decide upon their technical possibilities and finally their commercial results.

Of these problems the following are discussed as to their general meaning:

1. Availability and kinds of wood.
2. Diffusion and absorption.
3. Hydrolyzation with depolymerization and polymerizing dehydration.
4. Lignin problems.

4:40—12. Composition of Coconut Shells. L. C. Fleck, W. G. VanBeckum, and Geo. J. Ritter, Kimberly-Clark Corp., Kimberly, Wis. (Fleck), and Forest Products Laboratory, Madison, Wis., (Van Beckum and Ritter).

On account of the large lignin content, coconut shells should be a good source for charcoal. The extremely large pentosan content also suggests coconut shells as a

source for furfural. The acetic acid and the methoxyl contents compare favorably with those of hardwoods and suggest the use of the shells for the production of acetic acid and methyl alcohol by means of destructive distillation.

Since the shells have an extremely low percentage of stable cellulose and since their fibers are so minute, they would seem to be unsuitable as a source for cellulose for use in the cellulose derivative and the paper industries.

FRIDAY MORNING

9:00—13. Acid Pulping of Southern Pine—Sulfite Pulps for Viscose Manufacture. Charles Carpenter and Frank McCall, Pulp and Paper Laboratory of Savannah.

The paper covers the following topics: wood, pulping, bleaching, and preparation of yarn.

The wood of young longleaf (*P. palustris*), slash (*P. caribaea*), and loblolly (*P. taeda*) pines is pulped readily by the sulfite process. Pulps cooked to 40-43 per cent yield and to 1-2 per cent chlorine consumption are suitable for the manufacture of viscose. Characteristics of such unbleached pulps are: alpha contents of 87-90 per cent, cuprammonium viscosities of 50-100 centipoises (TAPPI), copper numbers of 2-3, and pentosan contents of 4-6 per cent.

Bleached in one or two stages the pulps have the following constants: alpha cellulose 87-90 per cent, cuprammonium viscosity 20-30, copper number 1.5-2.5, pentosans 4-5 per cent, brightness values of 80-88. The percentage composition of extractable matter—ash, Ca., Fe., and Cu. —depends upon equipment and methods employed in pulping and purification.

Strength, brightness and gloss of bleached and finished yarns from these sulfites compare well with similar characteristics of yarn produced under the same conditions from commercial rayon pulps.

9:30—14. The Effect of Pretreatment of Spruce Wood on the Reaction in the Sulfite Cooking Progress. D. C. Brown and F. E. Brauns, Institute of Paper Chemistry, Appleton, Wis.

Deresinified spruce wood meal before and after mild hydrolysis with 7 per cent oxalic acid is partially methylated by diazomethane. The lignins isolated from these wood meals have a methoxyl content of 20.4 and 21.6 per cent, respectively. The latter agrees with that of methanol lignin. Diazomethane methylated unhydrolyzed spruce wood cannot be delignified under the normal sulfite cooking conditions. Due to the removal of carbohydrates during the cook, the lignin content of the residual wood increases to 35.3 per cent. The recovered wood meal from this sulfite cook as well as the lignin isolated by means of 42 per cent HCl contains sulfur. This seems to indicate that in the sulfite cooking process the dissolution of the lignin occurs in two states: in the first stage addition of sulfurous acid on the lignin complex with formation of the so-called solid lignin sulfonic acid and in the second stage a rearrangement of the SO_3H group in the lignin complex with formation of the soluble lignin sulfonic acid takes place. In the diazomethane methylated spruce wood only the first stage takes place, for by covering of a specific hydroxyl group in the native lignin the rearrangement and, therefore, the dissolution of the lignin is hindered. Hydrolyzed spruce wood methylated with dimethylsulfate gives a methylated spruce wood with 35.3 per cent MeO which is about 4 per cent lower than that found for methylated unhydrolyzed spruce wood due to the removal of carbohydrates. It is not possible to isolate the methylated holocellulose from the methylated spruce wood since the methylated lignin cannot be removed by the Ritter-Kurth method with a simultaneous decomposition of the cellulose.

10:00—15. The Cooking Process. X. Pulping Wood with Alcoholic Nitric Acid Solutions. S. I. Aronovsky and Ross Aiken Gortner, University of Minnesota, St. Paul, Minnesota.

A series of cooks was made on aspen and jack pine sawdust and chips by refluxing with aqueous and alcoholic (ethyl and n-butyl) solutions of nitric acid followed by boiling the acid-treated wood with dilute caustic soda solutions. The concentrations of the acid and alkali, as well as the durations of the treatment, were varied. A number of cooks were also run with mixtures of aqueous and alcoholic nitric acid and with alcoholic solutions of sulfur dioxide and lithium bisulfite. The alcoholic nitric acid solutions gave much higher yields of good pulp than were obtained with the aqueous acid, under similar pulping conditions. Increasing the concentration of acid resulted in lower total yields but larger yields of screened pulp. Dilution of the alcoholic solutions with water had but little effect on the yields of pulp. Jack pine wood did not pulp as readily as the aspen. Sulfur dioxide and bisulfites in alcohol were not efficient pulping agents.

10:30—16. Pulping Bagasse with Alcoholic Nitric Acid. S. I. Aronovsky and D. F. J. Lynch, University of Minnesota, St. Paul, Minnesota.

A series of cooking experiments were carried out on bagasse using solutions of nitric acid in ethyl alcohol as the pulping agent, and the results were compared with those obtained by the use of aqueous nitric acid. Much larger yields were obtained with the alcoholic nitric acid. The latter is a good delignifying agent. The retention of Cross and Bevan cellulose, alphacellulose and pentosans was greater in the alcoholic nitric acid pulps than in those obtained by the use of the aqueous acid, under similar conditions of pulping. This is probably due to the inhibiting action of the alcohol on the hydrolytic activity of the dilute nitric acid.

11:00—17. Mechanism of the Reaction of Bromine with Furfural and Its Derivatives. Elizabeth E. Hughes and S. F. Acree, National Bureau of Standards, Washington, D. C.

The mechanism of the reaction of bromine in aqueous solution with furfural, methylfurfural, and furoic acid is discussed.

Bromine was liberated from a solution of 0.1 N potassium bromate-bromide by an equivalent amount of 0.1 N hydrobromic acid in the presence of one or one-half molar equivalents of the unsaturated compound. The consumption of bromine was followed at different periods of time by titrating the unused bromine and bromate as iodine with sodium thiosulfate. The corresponding acidity of the reacting solution was titrated with sodium hydroxide. This gave a measure of the bromine consumed and its equivalent of acid used in liberation of the bromine, and the hydrobromic acid regenerated.

Although bromine was apparently consumed by the olefine in the reaction, when one mole of bromine was allowed to react with one mole of furfural and the resulting product precipitated with 2,4-dinitrophenylhydrazine, the hydrazone showed no bromine on analysis. It is, therefore, postulated that bromine becomes bromide ions by removing electrons from the double bond and leaving it positive, as Myers, Clark and Acree demonstrated with ethylene and chlorine electrodes. At the positive double bond two OH from water are added subsequently, liberating two H^+ ions per mole of bromine consumed, thereby regenerating the acid used up in liberation of the bromine from bromate.

11:30—18. Studies of Cellulose Hydrolysis by Means of Ethyl Mercaptan. M. L. Wolfrom and L. W. Georges, Ohio State University, Columbus, Ohio.

The hydrolysis of solutions of high viscosity cotton linters in fuming hydrochloric acid at 16° during the first three hours has been studied in some detail. The course of the hydrolysis was followed by (1) optical rotation measurements; (2) mercaptalation with ethyl mercaptan at various time intervals; (3) preparation of the hydrolyzed-cellulose products corresponding to the same time intervals. Sulfur analyses of the mercaptalated products gave chain-lengths from 115 to 25 glucose units. These values compared favorably with those calculated from the cuprammonium viscosity data for both the mercaptalated and hydrolyzed cellulose, using the equation of Kraemer and Lansing.

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